BORON-BASED ADDITIVES IN OIL AND GREASE FOR WIND TURBINE APPLICATIONS

A Thesis

by

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ABSTRACT

This research investigates the tribological performance of crystalline and amorphous powders of boron as additives in lubricants: grease and mineral oil for potential applications of wind turbine. This research is focused on the wear resistance and lubricity performance of boron powders.

Experimental approach was used in this research. Several experiments were conducted including API RP 7A1 thread compound test, pin-on-disk tribometer experiment, stribeck curve analysis and surface analysis. It is possible to obtain fundamental principles of boron powder as additives in lubricants from these experiments.

The results indicate that amorphous boron powder is beneficial for lubricants additive, while crystalline boron powder showed that it is not proper as an additive, since there were a lot of traces of abrasive wear. According to the results amorphous boron powder provided anti-wear and better lubricity properties in the lubricants.

The observation and understanding obtained here will be beneficial for the lubrication industry. This research will provide basic principle of boron powder and possibilities of boron powder as additive in lubricants.

This thesis is composed of six chapters. The first chapter is about general ideas of lubrication from problems to emulsion techniques, followed by chapter II, motivation and objectives. Chapter III provides experimental details including boron powder's properties and basic information will also be discussed in this chapter. Finally obtained

results will be discussed in the chapter IV and V followed by chapter VI conclusions and future recommendations.

DEDICATION

This thesis is dedicated to my wife and parents, who have supported me with their faith and endurance. I also dedicate this thesis to my mother country for giving me this chance to study at Texas A&M University in USA.

ACKNOWLEDGEMENTS

First of all, I must offer my most profound gratitude to Dr. Liang, my advisor, for guiding and advising my research throughout the work. She graciously accepted me in her research group, even though I did not have a strong background in the tribology and mechanical engineering fields. I am also thankful for her insight and guidance, both directly and indirectly, when I encountered a challenge that I could not properly approach without advice. I learned a lot of different aspects from her such as: passion for research, kindness as well as a good heart to the students besides academic aspect.

Furthermore, I would like to show my appreciation to my committee member, Dr. Jacobs and Dr. Fang, for their guidance and suggestions for this research. They spend much time on my research and thesis, despite their busy schedule throughout the course of this study.

I am deeply indebted to the surface science group members particularly Carlos, Sung han, Huaping and Xingliang for helping me with every experiment. They were very busy with their research, and work, but they took the time to me, whenever I needed any kind of assistance from a fundamental aspect to knowhow of the solution. I could not have finished my thesis without their help and advice.

Even though I do not have enough experience and knowledge in surface science area, I can successfully finish my research. I am so lucky to have these people who have a lot of passion and knowledge in their work field. I learned both academic point as well as humane aspects in this surface science group.

NOMENCLATURE

μ	Coefficient of friction
η	Viscosity
h	Lubricate film height
s	distance of sliding
v	Velocity
F	Applied force
K	Specific wear rate
N	Speed
P	Pressure
V	Wear volume
S_1	Average slope of the first 8 runs of reference compound
S_2	Average slope of the 8 runs of test thread compound
S_3	Average slope of the second 8 runs of reference compound
BO	Break out
MU	Make up
COF	Coefficient of friction
FF	Friction factor
O/W	Oil-in-water emulsion
W/O	Water-in-oil emulsion

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CHAPTER I

INTRODUCTION

This chapter provides a brief background behind this research. With the development of machinery, interests have been focused on methods to reduce friction and wear for better efficiency and longer lifespan. For a wind turbine, researchers have been studying how to reduce friction and wear under high load specifically transmission and gearbox parts since the most failures occurred in those parts within 5 years, which is much shorter than the wind turbine's service life (20years) [1].

According to a recent study, in general, more than 30 percent of the machining parts need to be replaced every year [2]. With severe wear, a machine or a device is potentially fail that poses safety environmental danger. There are several ways to reduce wear, such as surface heat treatment, cold working by increasing hardness, and selection of a harder material. These methods are usually high costs [3]. Developing a better lubricant is an economical approach.

Lubricants such as grease and mineral oil are widely used in applications related to tribology: machine parts, engine, transmission, drilling and bicycle gear, among others. In a wind turbine, in particular, it needs both lubricating oil and grease, since it comprises of various machining parts including bearings, drives and gear boxes. Because, different machining parts are requiring different lubricant types. It is attributed from the properties of each material. For example, grease is not proper for high speed applications, while oil can be used for any kind of applying speed.

A typical lubricant is comprised of a base oil and additive. The base oil provides fundamental properties of lubricants while additives provides increased specific performance such as extreme pressure endurance, anti-corrosion, anti-oxidation, and dispersion. An important factor is that the lubricant's capability is closely interrelated to the additives. If an additive shows a good lubricity is added to the lubricants, the lubricant's performance will be increased as well.

In this chapter, a brief introduction to tribology will be given. Lubrication of three different lubrication regimes and four types of lubricants will be discussed. In the last part of this chapter, the emulsion technique will be discussed.

1. 1. Tribology

Tribology is a study of the physical and chemical interactions of surfaces between two or more objects that have relative contact movements. In other words, tribology is a generic term for practical science technologies that related to the friction, wear and lubrication in relative motion of interacting surfaces. The term tribology was firstly used in UK in 1966 and was derived from Greek word "tribos" which means rubbing. The physical meaning of tribology is that it is a practical study of the friction phenomenon that is caused by relative contact friction movements [4, 5].

In ancient times, the first recorded use of lubricants was with olive oil. In history, olive oil was used to move large stones to make pyramids. Like olive oil, animal fats were used as an old form of grease. These natural based lubricants were frequently used throughout ancient history until the 19th century because those were easier to obtain.

Along with the development of oil industry, petroleum-based lubricants have become standard use in every field of industry after 1859. Lubricant additives including sulfur were first introduced in the early 20th century. They were commonly used in base oils for improving the lubricant's performance after the 1930s due to the development of more complicated engines and machinery [6].

Traditional lubricants and additives could not provide proper protection for contact surfaces under the extreme pressure and temperature. Because of this, solid lubricants began to emerge during the 1940s. Graphite, molybdenum disulfide and lubricating plastic were the most popular solid lubricants due to their stability at high temperature and ease of use [7].

Since petroleum-based lubricants are harmful to the environment and people, it is obvious that the bio-based lubricants have been favored among researchers for 20 years. These lubricants should be rapidly biodegradable and nontoxic. There are two types of bio-lubricants: vegetable based oil and synthetic esters oil which came from the mineral oil based products [8].

1. 1. 1. Energy loss due to friction

As listed above, mankind has been developing lubricating materials since the ancient times. It is because they understand that there will be not only enormous costs needed to replace or repair worn parts, but also worn components are a threaten to people. Wear phenomenon or also known as abrasion, can be defined as materials that have deviated from the contact surfaces when two or more objects that are undergoing relative contact movements. Problems related to the wear phenomenon are listed below [4].

1) When substances are coming away from the surface, the dimension will be changed from the original shape and then the clearance of the contact surface will be different in size automatically. As a result, there are big differences in the machinery device’s sealing effect and assembly tolerance from the time of assembling.
2) The liquidity of the working fluid will be decreased due to the occurrence of wear particles and in some cases, wear particles can cause serious damage like blocking up the nozzles or fine clearances.
3) The quality of the products in the industry could be affected due to large or small particles generated from the cutting or molding tools [9].
4) A small amount of wear is inevitably occurred in the frictional surface. However, fast-paced or unexpected wear are shortcuts to reducing the machinery’s life or increase the product defect rate. Therefore, it is required to use wear resisting material or increase the hardness of the surface by through the surface-modifying process [10].

As listed above, friction and wear are major problems in operating machines, robots and vehicles in the industry. Every machining parts, gears and engines will need to be replaced in a timely manner before it fails. High friction is directly related to the high wear rate and rapid break down. Major breakdown costs are shown table 1-1 [2, 11].

Table 1-1. Annual major breakdown costs in USA [2, 11].

Classification	Cost($)	Classification	Cost($)
Ball Bearing(US)	240 billion	Automotive Industry	69.85 Million
Drilling Bit(each)	125,000	Shipping Industry	5.42 Million
SAG Mill(each)	25.3 million	Energy(electric)	5.63 Million

As mentioned earlier, reduction in friction can increase the operation efficiency and it is a low-cost approach. In table 1-2, it introduces potential savings by following tribological practices [12].

Table 1-2. Potential savings from tribological practices [12].

Classification	Potential Improvement
Maintenance and Replacement	45%
Breakdown Losses	22%
Higher Efficiency	4%
Increasing Life span	20%

1. 1. 2. Replacement costs for wind turbine parts

This section will provide the information about lubricating related loss in a specific field: a wind turbine that needs both oil and grease based lubricants. This is because a wind turbine is highly technology-intensive powder plant that is comprised of diverse mechanical parts: 4 different bearings, 2 different drives, and 3 different gear boxes [13].

According to R. Kewitsch, the unplanned operating cost of wind turbines are much higher than planned one, which implies that the sudden failure of mechanical parts requiring significant cost as shown in table 1-3 [14].

Table 1-3. Operating costs of replacement of wind turbine parts [14].

Operator	# of turbines	Duration of service	Failure parts	Costs of unplanned replacement($)	Costs of planned replacement($)
EnviaM	15	5 years	3 gear boxes	531,000	132,700
E. disnatur	130	5 years	12 gear boxes 40 generator bearings	6,056,000	1,514,000
Juwi Manage- -ment	59	3 years	20 gear boxes 1 generator bearing 1 main bearing	3,684,600	921,100

A service life of a wind turbine is about 20-25 years. However, there are always sudden failures of machining parts of a wind turbine. Some failures could be happened less than 5 years or even less than several months as shown in table 3. Sudden failure of a small piece of a bearing could cause small amount of replacement fees or huge costs to change gear box or generator even a wind turbine itself as shown above table. A bearing failure affects not only maintenance costs but also losing revenues from malfunctioning of a wind turbine [15].

Frontier Pro Service reported that the most gear boxes' failures occurred by poor lubrication and improper lubricant selection combined with lack of maintenance. Usually oil is used for gear box lubrication, while grease is used for different types of bearing. High load carrying capacity and excellent wear resistance are the most favorable properties for wind turbine lubrication. Therefore, it is recognizable that better lubricating oil and grease can increase the service life of a bearing, gear box ultimately wind turbine itself [16].

1. 2. The roles of lubrication and its regimes

Lubrication is used to reduce friction by applying oil and grease which prevents the generation of heat and wear on surfaces. Various types of oil and grease are used as lubricants to reduce the friction from affecting the surfaces physically allowing them to slide against each other without coming into contacts. Therefore, it is possible to reduce wear and friction between two parts. In addition, lubricants give other advantages not only preventing contaminants and corrosions, but it also provides less power loss. It should be noted that there is always wear debris, or contaminants, in the working contact area and these materials are enough to affect machines and their working parts. Lubricants act like sealants which provide proper protection from wear debris, contaminants and oxidation [17].

There are three different types of lubrication regimes: Boundary lubrication, mixed lubrication, and hydrodynamic lubrication regime categorized by film thickness and surface roughness. The variation of coefficients of friction is shown in figure 1-1.

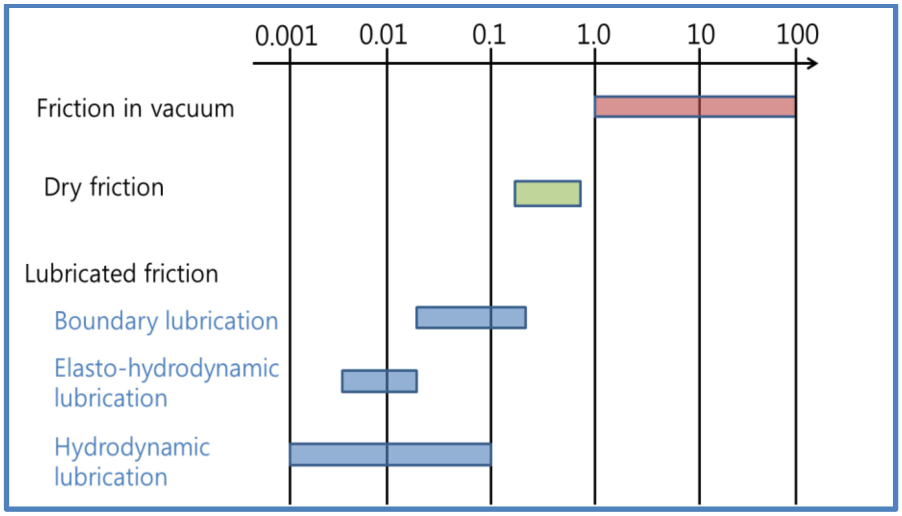

Figure 1-1. Variation of coefficient of friction in different lubrication system [10].

The coefficient of friction is dramatically changed depending on different speeds and loads in each lubrication type as shown in the Stribeck curve in figure 1-2. This curve was named after Richard Stribeck (1861-1950) who had a great notable achievement for friction and lubrication in the German Federal Institute for Materials Research and Testing. He studied the variation of coefficient of friction using different loads and speeds. He published his test results on September 6 1902. After 10 years, Gümbel used a dimensionless lubrication parameter $\eta N/P$ (where η is the viscosity) which on Stribeck's curve against the coefficient of friction [18, 19].

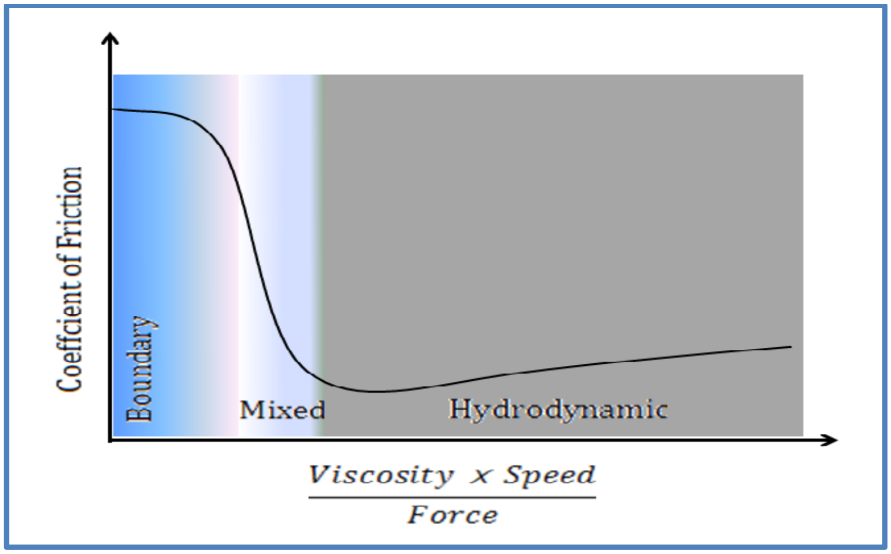

Figure 1-2. Stribeck Curve [19].

1. 2. 1. Boundary lubrication

In the Boundary Lubrication regime, severe surface contact still occurs while an oil film is provided to the contact surface as shown in figure 1-3. But a surface film that can reduce wear and friction can be generated. In this case, the friction coefficient is usually ranges from 0.1 to 0.3 [12]. Four different types of wear can be created in the boundary lubrication regime: adhesive, abrasive, surface fatigue and chemical wear [17].

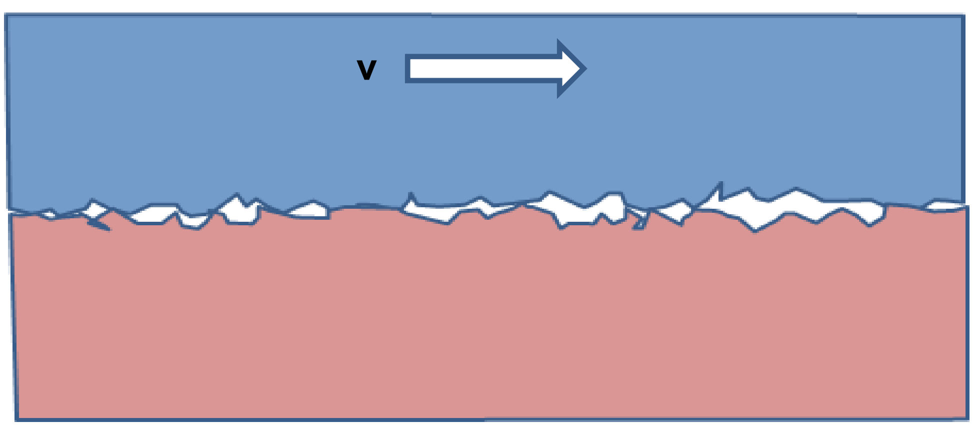

Figure 1-3. Boundary Lubrication.

1. 2. 2. Mixed lubrication

In mixed lubrication, there are intermittent contacts with the surface asperities and there is a partial fluid lubrication as well shown in figure 1-4. At this time, the friction coefficient is between 0.03 and 0.1 accompanying slight wear of the contact surface [12]. In the mixed lubrication regime, there will be some contact areas between two different sliding surfaces which mainly occurred during the low speed conditions, particularly start-up and switch-off periods. During this term, softer parts of the contact areas will be plastically deformed and worn [18].

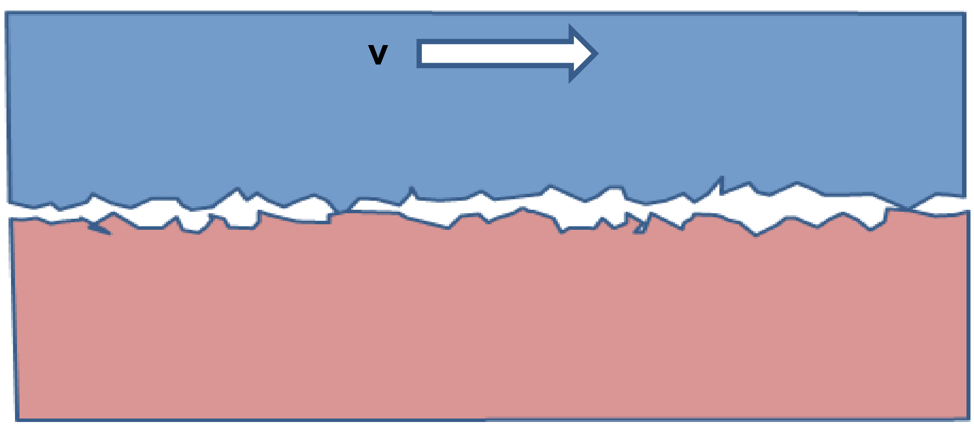

Figure 1-4. Mixed Lubrication.

1. 2. 3. Hydrodynamic lubrication

Hydrodynamic lubrication is the regime where contact surfaces are completely separated by the lubricant fluid. In this case, a load on the contact surfaces will be supported by the hydraulic pressure that is caused by the relative motion of the contact surface. Therefore, the wear of the contact surface is very small and the friction losses are only within the lubrication film as shown in figure 1-5. In the case of hydrodynamic lubrication, the minimum oil film thickness is about 0.008 to 0.02 and the coefficient of friction is under 0.03 [12]. The film thickness will increase along with decreasing the load. It also will increase with increasing the viscosity and rotation speed. There are several factors that affect film thickness in hydrodynamic lubrication regime.

1) It is important that the angle between surfaces is small enough to form a lubrication wedge.
2) The lubricant's viscosity should be high in order to maintain proper thickness and carry the load.
3) To maintain the hydrodynamic film, the operating speed must be high enough.

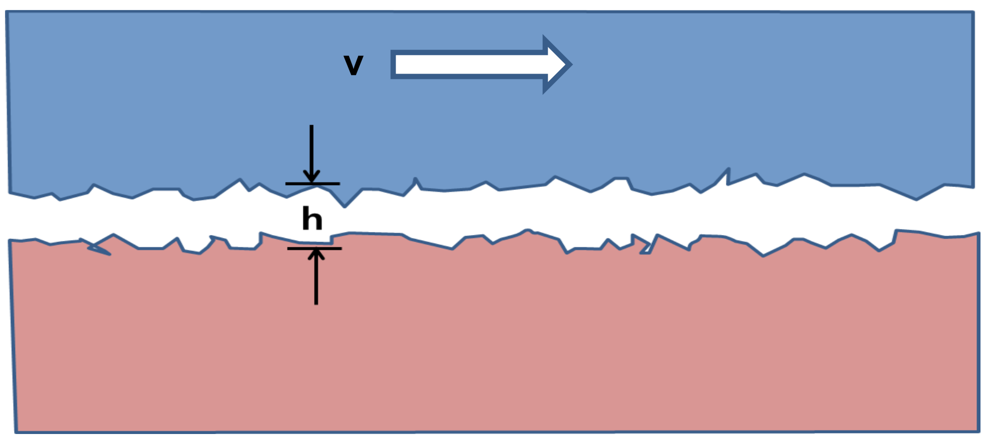

Figure 1-5. Hydrodynamic Lubrication.

1. 3. The types of lubricants

As mentioned earlier the purpose of lubrication is to reduce damage on surfaces by generating thin film which has low shear stress between two objects. Depending on places of usage, methods of usage and the kind of friction, there are four different types of lubricants: liquid lubricants, semi-solid lubricants (grease), solid lubricants and gas lubricants depending on places of usage, methods of usage and the kinds of friction [20].

1. 3. 1. Liquid lubricants

Liquid lubricants are used in almost every application from industrial usages to households. Animal and vegetable oil were used for lubrication in the past. However, it has been possible to make high quality lubricants from crude oil thanks to the development of the petroleum industry. Because of that, it is not an exaggeration that most of the liquid lubricants are mineral oil, which came from petroleum oil.

Synthetic oil is commonly used for extreme conditions. It is a kind of mineral oil that is artificially modified by controlling its chemical compositions. Most synthetic oils come from crude oil but it could be made with other raw materials. As shown under the 1-4, additives may be used for different purposes for the liquid lubricants [6].

Table 1-4. Additives for liquid lubricants [6].

Additive type	Compound	Function
Extreme Pressure	Sulfur contained compounds	Increase load carrying capability
Antiwear	ZDDP (Zinc dialkyldithiophosphate)	Increase load carrying capability Reduce three body wear
Antioxidant	ZDDP (Zinc dialkyldithiophosphate)	Formation of sulfur film
Anticorrosion	Fatty amines and polyamines	Form a mono-molecular film or layer
Dispersant	Polyisobutylene Succinimide	Stabilize small colloidal particles

Oil is a representative of liquid lubricants while grease is a representative of semi-solid lubricants. The difference between them is that oil consists solely base oil and additives while grease consists of base oil, additives and thickeners. Grease's nature is changed from liquid to semi-solid by adding a thickener. It is important to choose proper lubricant types to use in different conditions. Table 1-5 indicates the usages of lubricant types between grease and oil.

Table 1-5. Differences between oil and grease.

Division	Oil	Grease
Rotational speed	Can use every speed	Unable to use under high speed
Rolling resistance	Small	Relatively higher at the beginning
Cooling effect	Large	Small
Diffusible	More	Less
Maintenance period	Relatively short	Relatively long
Sealing device	Complex	Simple
Leakage	More	Less

1. 3. 2. Semi-solid lubricants

This research focused on grease, which is widely known as a semi-solid lubricant. It has been generally used for machines and gears, especially high loads and low speed components. Grease is a blended material based on oil with some thickeners and additives mixed in it to improve its performance. There are several advantages to using grease as a lubricant. First of all, grease is very convenient to apply. Second, it is very cost effective and it has a seal property that can prevent contamination from external environments. As shown in the Figure 1-6, usually grease is composed of 70~90% base oil, 5~25% of thickener and 0.5~10% of additives. However, some greases show quite different composition ratios depending on purposes [18].

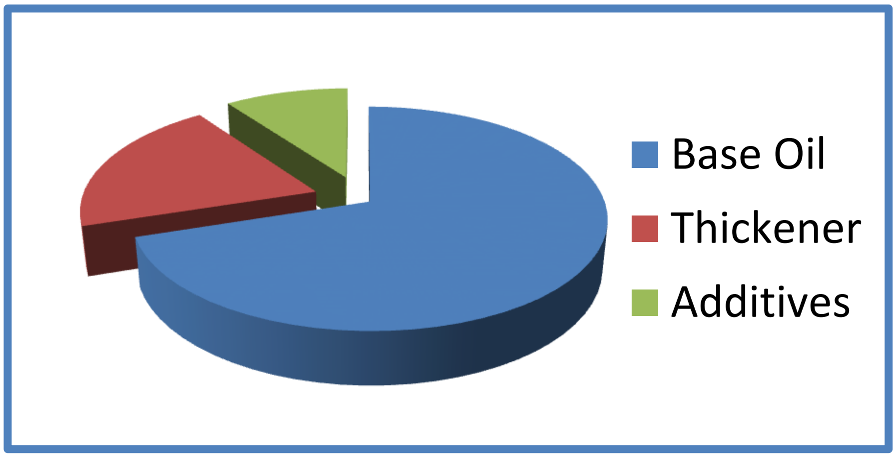

Figure 1-6. Composition of grease.

1. 3. 2. 1. Base oil

As seen in the previous figure 6, base oil is composed of 70~90% grease which dramatically affects the grease's properties listed below [21].

1) Operating temperature range.
2) Heat resistance.
3) Torque.
4) Durability.
5) Anti-resinoid.

There are several types of base oil being derived from crude oil, chemical synthesis, and other natural resources. Each type of base oil has different advantages and disadvantages. Mineral oil was the primary lubricant used, but synthesized oil and natural oils have recently become popular since people are now taking the environment into consideration [22]. The pros and cons of different types of base oils are listed in the table 1-6.

Table 1-6. Comparison between synthetic oil and mineral oil [22-24].

Classification	Type	Advantage	Disadvantage
Synthetic oil	Olefinic	Anti-resinoid, low flow point	Lower lubricity than ester base oil
	Ester	Lubricity, stability of the contact resistance	Low anti-resinoid Low anti-rubbery
	Silicon	Oxidation stability, Anti-resinoid	High price, low lubricity
	Fluorine	Oxidation stability, Lubricity, Anti-resinoid	High price
Mineral oil	Paraffinic	Lubricity	Low oxidation stability

1. 3. 2. 2. Thickener

Thickener is a material that can increase the viscosity of a solution or a liquid/solid mixture without changing its properties. Metal-salt soap is the most commonly used thickener in grease. Metal-salt soap is made by fat or fatty acids that could be obtained from any material such as animals, vegetables, and marine lives [25]. Simple and complex soaps are currently being used for grease. A simple soap is made up by fatty acids. A complex soap means that the soap crystals and fibers in which the soap is made from crystallization of two or more compounds. In these days, there are several types of grease thickeners being used [26]:

1) Aluminum and Aluminum complex
2) Calcium and Calcium complex
3) Lithium and Lithium complex
4) Polyurea

1. 3. 2. 3. Additives

Grease shows its lubrication ability without additives, but different types of additives are used in order to meet the performance requirements of the user. Additives can enhance grease's chemical characteristics as well as physical performance. Furthermore, it can also increase the service life of grease by minimizing wear, corrosion and rust damage on lubricated metal surfaces. Several types of additives are shown in table 6. Other additives are used to: improve oiliness for increased lubricity, stabilize structures, prevent the scattering of grease and increase adhesion.

As shown in figure 1-7, according to recent usage, 0.5% to 10% of additives are used to enhance grease properties. It is important to choose proper additives for different circumstances and parts [27].

Table 1-7. Different types of additive in semi-solid lubricants [26].

Additive type	Compound	Function
Extreme pressure / Anti-wear	Sulfurized olefins Chlorinated paraffin Metal soaps, including lead Solid additives	Increase load carrying capability Reduce three body wear
Anti-corrosion	Carboxylic acids Fatty amines Metal sulfonates	Form a mono-molecular film or layer
Anti-oxidant	Hindered phenols Aromatic amines Metal dialkyldithiophosphates	Formation of surface film or layer
Lubricity and adherence	Fatty amides, fatty acids, partial esters, polymeric esters Animal and vegetable fatty oil	Maintaining a physical boundary between contacting surfaces
Solid particles	Molybdenum disulfide, Graphite, Boron nitride, Zinc oxide	Thickener, increase load carrying capability

1. 3. 3. Solid lubricants

Solid lubricants can be used in place where conventional lubricants (oil and grease) are unsuitable. This type of lubricant has low shear strength which provides a lower coefficient of friction and high compression strength that gives high load carrying capability [7]. There are three types of inorganic compounds typically used as solid lubricants. The first is layer lattice solid materials such as graphite and molybdenum disulfide whose crystal lattice structures are arranged in layers. The second is a soft solid like: white-lead, lime, silver iodide, talc, bentonite, etc [27-28]. The last is chemical conversion film. Many inorganic compounds can be generated on a metal surface with chemical reactions. Sulfides, oxides, phosphates and oxalates are known compounds used for this type [29].

1. 3. 4. Gas lubricants

Gas lubricants have an advantage of being used under a wide range of temperature (-200℃ ~ 2000℃). Liquid and semi-solid lubricants have difficulties under such extreme conditions due to the thermal expansion and wear problems. Gas lubricants are typically used at high-speeds and low-loads while solid lubricants are used for low-speeds and high-loads terms. Gas lubricants and liquid lubricants have similar principles. The viscosity of gas is much smaller than that of liquid, but it has a much larger compressibility. Thus gas lubricants have thin films and less load capacities [30].

Devices dealing with various types of gases are often desired, because they simplify the machines and parts. Gas lubricants are used in various other ways such as reducing pollutants that may be caused by other lubricants. Gas, air, steam, industrial gases and liquid metal-vapor are currently using in this manner [4].

1. 4. Emulsion techniques

For the friction test, an emulsion technique was used, without using the emulsion techniques, boron could not be mixed with the mineral oil as shown in figure 1-7.

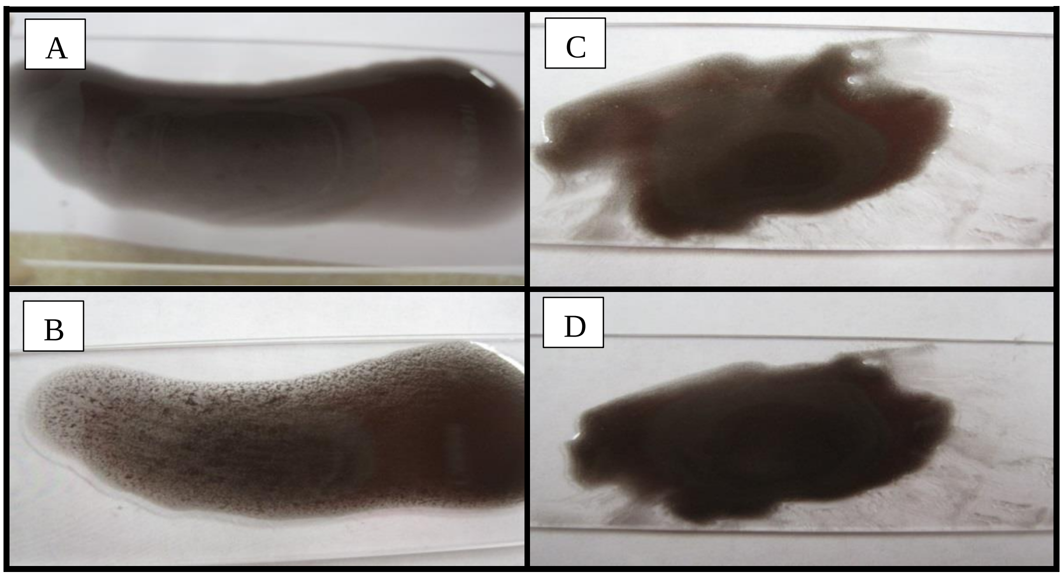

Figure 1-7. Reason for emulsion.

Figure A and C are right after mixing, and figure B and D are 10 minutes later pictures. Figure A is just mineral oil and oxidized boron powder mixture, 10 minutes later, the boron powder is agglomerated, while there was no difference in the case of emulsion as shown in figure C and D. However, boron powder is well mixed with water, for that reason, boron powder can be dispersed in the mineral oil, once it is mixed with water using emulsion technique.

The emulsion is a mixture of two immiscible liquids, like water and oil, as shown in figure 1-8. It is widely recognized that water and oil are immiscible, but when an emulsifier is added, they can be mixed together. The reason that they cannot be mixed without an emulsifier is that water has polar structures that contain both positive charges and negative charges at either end, while oil consists of carbon chains and does not have a polar structure causing oil and water to remain separate from each other. In other words, the only way to blend these two liquids is to add a specific emulsifier.

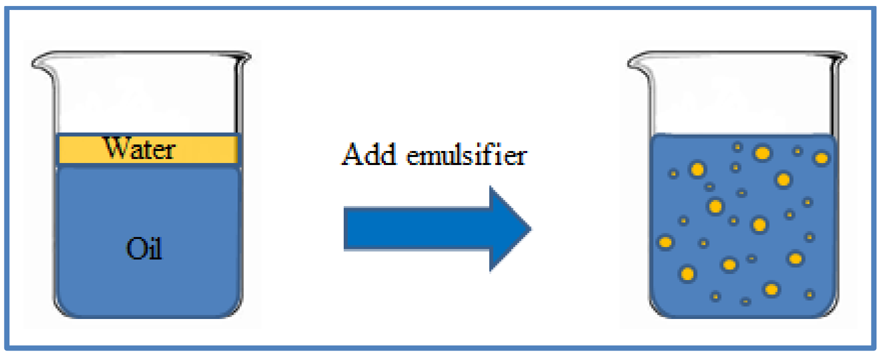

Figure 1-8. Typical emulsion diagram for water and oil mixture.

A structure of the emulsifier is provided in figure 1-9. The emulsifier is an amphiphilic molecule that comprised of two different parts: hydrophilic head (water loving) and hydrophobic tail (water hating). These reduce the surface tension between the oil and the water allowing both molecules to be mixed together [31].

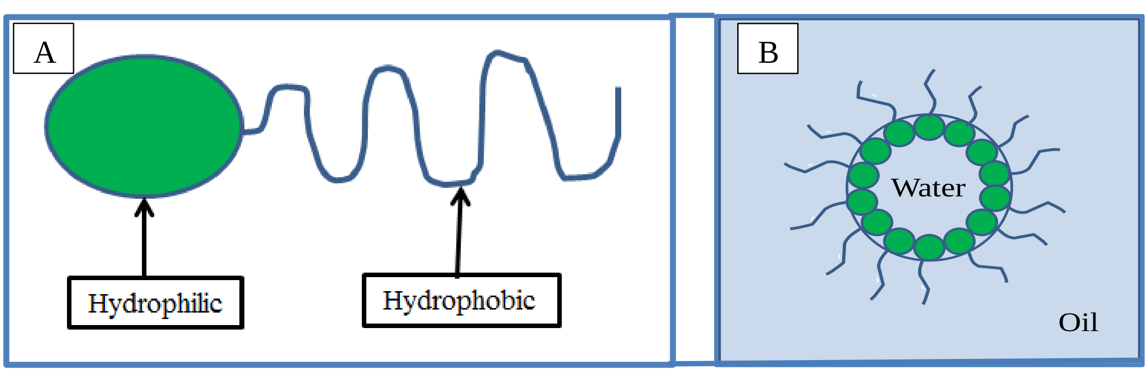

Figure 1-9. A structure of an emulsifier [32].

There are two types of emulsions: water-in-oil (W/O) emulsion and oil-in-water (O/W) emulsion depending on the type of emulsifier. As the name indicates, if water is dispersed in oil, it is called water-in-oil emulsion and vice versa. Water-in-oil emulsion is used in this research, because the amount of oil has to be higher in order to increase the lubricity. On other word, higher amount of oil is needed to make relatively good lubricant. It should be noted that the water is very slowly added into the oil in order to make water-in-oil emulsion [33].

In table 1-8, the emulsifiers are categorized under: water-in-oil emulsifier or oil-in-water emulsifier depending on the Hydrophile-Lipophile Balance (HLB) value indicated by the surfactant's degree of hydrophilic or lipophilic tendency. The HLB value ranges from 0 to 20. If the value is over 10, the material is water soluble and values less than 10 are soluble in oil. The HLB value required is between 3~6 for water-in-oil emulsion. Sorbitan stearate was used as an emulsifier with the concentration varying between 1% and 4%.

Table 1-8. HLB value depending on the emulsifier types.

Emulsifier Type	HLB value	Typical Kind(HLB value)
Water-in-oil	〉10	Sorbitan Stearate(4.7) Lecithin(4.0) Polyglyceryl Oleate(5.0)
Oil-in-water	〈10	Cetearyl Glucoside(11) Oleth-10(12.4) Polysorbate 60(14.9)

Emulsion has a lot of advantages and it has been widely used in various fields in modern society from the drug industry, food products, lubrication and the crude oil purification industry as shown in table 1-9.

Table 1-9. Application areas of the emulsion technique [34-36].

Application Area	Required Emulsion Property
Drug, Cosmetics	Biocompatibility, Non-toxic
Food products	Edible, Non-toxic
Lubrication	Chemical stability, Adsorptivity, Low price
Crude oil purification	Ease of deemulsion

1. 4. 1. Emulsion in lubrication

Emulsion is widely used for various applications as mentioned earlier. It can also be used for lubrication, because it shows better characteristics in terms of fire resistance and low costs, since it contains certain amount of water. It should be noted that there are several other advantages of lubricating emulsion: higher machining speeds, less smoke emissions and cleanliness of the work environment [37]. For this research, water-in-oil emulsion was used for better lubricating ability. The amount of components used in this research as follow: mineral oil (heavy) 75wt (%), 19.5wt (%) of water, 0.5wt (%) of emulsifier and 5wt (%) of oxidized amorphous boron powder. The boron powder was mixed with hot water and the mixed water was poured into the mineral oil slowly.

CHAPTER II

MOTIVATION AND OBJECTIVES

As discussed in Chapter I, base oils and additives are the main components of grease and oil. The base oil provides the fundamental properties of the lubricants: viscosity, flash point, volatility and solubility, while additives improve specific functions in the lubricants: extreme pressure, anti-wear, anti-oxidant, anti-corrosion and dispersion.

Each lubricant contains at least one, or more, additive in order to meet the user's requirements and the additives' composition are varying from 0.5% to 10% depending on the lubricants usage. An important aspect is that lubricants' performance is directly related to the additives, if proper additives are added into a lubricant, the performance of the lubricant could be increased as well.

This research focuses on the crystalline and amorphous boron powders' tribological performance such as anti-wear and extreme pressure endurance, when the powders added into lubricants.

The objective of this research is to develop potentially new lubricant additives to oil or grease. Experiments will be conducted in order to evaluate and understand the mechanisms of boron in lubricants. There are two main goals of this research:

1) Obtain understanding in lubrication properties of crystalline and amorphous boron powder in grease.

2) Obtain understanding in effects of boron additives on lubricating mechanisms in a liquid lubricant.

These objectives are important to understand the boron powders effect and mechanism in lubricants. This research is based on two different experimental approaches: API RP 7A1 thread compound tests and pin-on-disk tribometer experiments. These tests will provide the information of boron powders roles in different lubricants: grease and oil.

Throughout this research, it is possible to obtain the new knowledge of boron powders' frictional and wear protection mechanisms in lubricants.

CHAPTER III

EXPERIMENTAL DETAILS

This chapter discusses materials and experimental approaches used for this research. Crystalline and amorphous boron powders were used as lubricant additives. Experimental approaches are composed two different devices: API RP 7A1 thread compound test machine and the tribometer (CSM instrument). The Calcium fluoride bolt lube standard formulation and the Super Lube grease (commercial product) will be used for the grease tests, while a mineral oil (heavy) obtained from Sigma-Aldrich will be used for a Pin-on-Disk tribometer tests. Various other surface observation devices and Raman spectroscopy were used for understanding the lubrication mechanism of boron powder.

3. 1. Test materials

3. 1. 1. Boron

Boron is a metalloid whose atomic number is 5. Its name comes from the Persian "burah," which indicates borax. Boron is one ingredient of borax and its elemental symbol is B. Borax has been widely known since ancient time and it has been used to make glass and detergents.

3. 1. 1. 1. History of boron

From A.D. 300, borax glazes were used in china and there are a lot of reports that Egyptians, Tibetans and Arabians used boron materials. In the 13^{th} century, Marco Polo took glaze into Italy. Boron exists as a compound in nature and boric acid is the most common type [5]. Boric acid has been used for medicinal purposes since it was discovered in 1777 near Florence, Italy. Pure boron products were not discovered until 19th century when Humphry Davy, Louis Jacques Thenard and Louis Gay-Lussac made pure boron by a reduction process of boron trioxide with potassium. They sent electric currents to the solution of borates and they found a brown precipitate which indicated that the produced element was amorphous boron particle. Much later in 1909, pure boron was prepared by American chemist Ezekiel Weintraub [38-39].

3. 1. 1. 2. Properties

Boron does not exist in the nature as a pure form but it can be found as compounds form like Sassolite (H_3BO_3), Colemanite ($Ca_2B_6O_{11}$), Boracite ($Mg_7B_{10}Cl_2O_{30}$) and Kernite ($Na_2B_4O_7$) [39]. General and physical properties of boron are shown under table 3-1.

Table 3-1. General and physical properties of boron [5].

General Properties		Physical Properties	
Atomic Number	5	Phase	Solid
Atomic Weight	10.811	Liquid Density at m.p.	2.08g·cm^{-3}
Electron Configuration	[He]$2s^2 2p^1$	Boiling Point	3927℃
Group	13	Melting Point	2076℃
Element Category	Metalloid	Heat of Fusion	50.2kJ·mol^{-1}
Electrons per shell	2, 3	Heat of Vaporization	480kJ·mol^{-1}

Boron has a similar stability of covalent bonds with carbon in the molecular network. Amorphous boron is combined randomly including icosahedra symmetry. Crystalline boron is hard materi al with black color. The melting point of the crystalline boron is over 2000℃. Boron has four kinds of polymorphs: α, β, γ and T as shown in table 3-2. α, β and T phase is based on the B_{12} icosahedra while γ phase is based on B_2 atomic pairs and rock salt arrays. These boron phases can be made under 12~20Gpa of pressure and 1500~1800℃ of heat. After that moment, boron became stable to the heat and pressure. α, β phases are coexisting in a standard state, β phase is a little more stable. When pressure is applied to boron at least 160Gpa, it became the superconductor at 6~12K temperature and the structure of boron phase is yet known [38, 40].

Table 3-2. Different phases of boron [41-44].

Boron phase	α	β	γ	T
Symmetry	Rhombohedral	Rhombohedral	Orthorhombic	Tetragonal
Vickers hardness(Gpa)	42	45	50~58	
Bulk modulus(Gpa)	185	224	227	
Bandgap(eV)	2	1.6	2.1	

3. 1. 1. 3. Applications of boron

As mentioned above, borax is one of the compound forms of boron and it has been widely used as a disinfectant or a cleaner since it shows detergent and water softening properties. It also used to make borosilicate glass [5]. Sodium perborate, a compound form of boron, is used for detergents or fiberglass insulators for major industrial uses. Boron polymers or ceramics have the roles of high-strength lightweight structures or refractory materials.

If boron compounds are added to the silicon-based glasses and ceramics, then it helps to have thermal shock resistance for those materials. Boron occurs in two isotopes in the nature: ^{10}B and ^{11}B and both elements' natural abundance are different from 18.83% and 81.17% respectively. The isotope boron-10 is used for neutron-trapping reagent [45].

In biology, borate shows little toxicity in mammals but it is used for pesticides since it shows toxicity to the arthropod. Boron is indispensable for animals and plants; boron compounds strengthen the cell walls of all plants even a little amount. It is believed that boron is only 0.0001% of weight but it has a very important role even though its physiological role is not known in animal experiments [40].

It is expected that Sodium Borane can be an alternative compounds which stores hydrogen in the development of a fuel cell. In regards to the hydrogen storage, there is a lot of research still in progress. In addition, when boron is combined with magnesium, it could turn to the form of a superconductor which can be utilized to the electric / electronic parts such as maglev trains, underground power transmission cables and digital devices [40].

3. 1. 1. 4. Occurrence

There are over 200 minerals that contain boron. The most important and most actively traded minerals are Kernite ($Na_2B_4O_7 \cdot 4H_2O$), Tincal ($Na_2B_4O_7 \cdot 7H_2O$), Colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) and Ulexite (NaCa$B_5 9 \cdot H_2O$). Boron can be deposited as skarn with limestone or may be formed as a by-product of volcanic eruptions, but most important borate deposits are formed by chemical precipitation in the basin of the playa type [5]. In addition, borates also exist everywhere at low concentrations such as in rocks, soils and waters. Table 3-3 indicates the concentration of borates per Kg in each material [38, 40].

Table 3-3. Boron content in different material [38, 40].

Source	Weight (%)	Source	Weight (%)
Earth's crust	1 x 10^{-3}	Iron ores (maritime)	5 x 10^{-2}
Rocks	1 x 10^{-4}	Iron oreos(nonmaritime)	5 x 10^{-4}
Acid Rocks	1.5 x 10^{-3}	Lime stones	5 x 10^{-4}
Soils	1 x 10^{-3}	Meteorites	3 x 10^{-4}
Granite pegmatites	$(1-10)$ x 10^{-3}	Sea water	1.5 x 10^{-2}
Marine clays	5 x 10^{-2}	Salt springs	$(3-20)$ x 10^{-3}
Sedimentary rocks	1.2 x 10^{-2}	Salt lakes	$(1-60)$ x 10^{-2}

There are several countries only have significant boron reserves as shown in table 3-4. The international market for borates is approximately 42million tons and mainly from Turkey, the United States and South American nation (Argentina, Bolivia, Chile and Peru). China and Russia also produce significant amount of borates, but they export very little for the international market. The world's largest production companies are Turkey's Eti Bor Inc. and U.S borax Inc. They supply about 74~80% of worldwide consumption [40].

Table 3-4. Reserves of boron in the world [38, 40].

Country	Reserve (million tons)	Country	Reserve (million tons)
Turkey	563,000	Chile	41,000
USA	80,000	Bolivia	19,000
Russia	100,000	Peru	22,000
China	36,000	Argentina	9,000
Kazakhstan	15,000	Iran	1,000

3. 1. 1. 5. Possibilities of boron powder as an additive

Boron nitride is the best known additive among boron compounds since it has lamellar structures like graphite and MoS_2. There are several types of boron additives for coatings and boundary lubrication additives. Two different types of boron compounds were used as anti-wear and extreme pressure additives in the Choudhary and Pande's research [46].

They used organoboron and inorganic boron salts, both possessing different properties. Organoboron is dissolved in mineral oil while inorganic boron salts are dispersed in the base oil. Similar to those additives, borate was used as an additive for ester and mineral oils in Kreuz's research [47]. He found that borate improved the load carrying capability and that there was a thick tribofilm generated after operation. As discussed so far, different types of boron compounds have proved their lubricating abilities. However, the possibility of pure boron as an additive has not been discussed yet.

This research focuses on the performance of amorphous and crystalline boron powders as additives in grease and mineral oil. Even though their elements are the same, they show different characteristics which imply that there should be differences or gaps in terms of lubrication capability.

The differences between the properties of crystalline boron powder and amorphous boron powder will be discussed below but it should be noted that boron trioxide glass is composed of planar BO_3 triangles while crystalline boron powder has less oxygen impurities. In addition, several authors insisted that boroxyl rings, whose structure is 2D plane as shown figure 3-1, are found in the boron trioxide glass when glassy boron powder is oxidized. It is believed that both planar structures of glassy boron powders may be good in the lubricants [48].

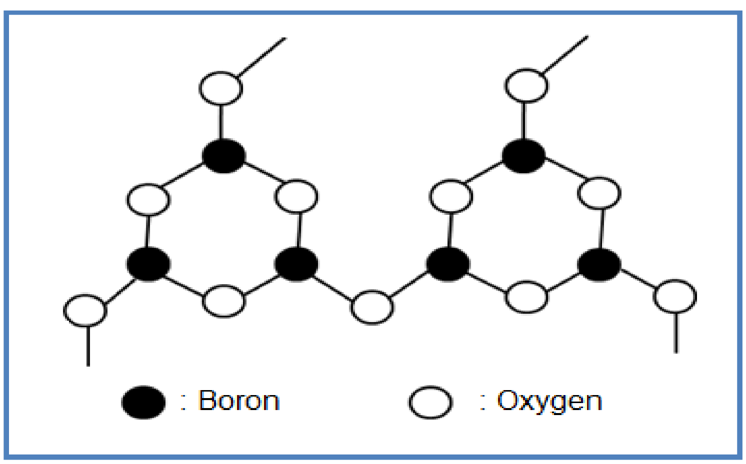

Figure 3-1. Two boroxyl ring configuration [36].

Furthermore, amorphous boron powder can be oxidized in the atmosphere naturally and it has a strong tendency to form boric acid on its surface when it is exposed to the humid air or water [49]. As known, boric acid has a layered structure with weak interlayer bonding which is good for lubrication as shown in figure 3-2 [50]. Although the amount of boric acid is not known, it will still show some lubrication ability in this research. This research will be focusing on both boron powders' tribological performance in lubricants as additives.

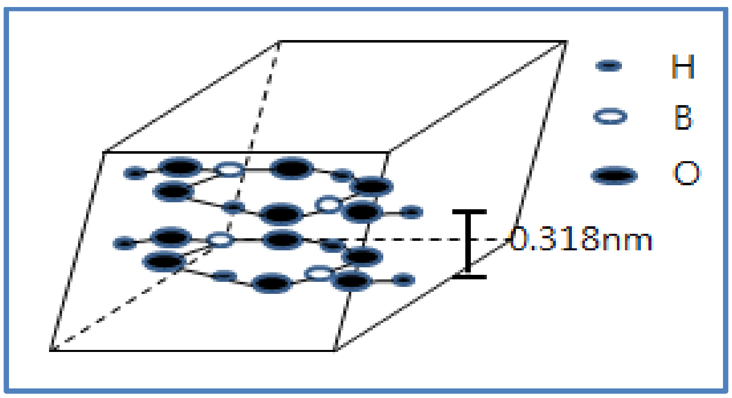

Figure 3-2. Boric acid in triclinic crystal structure [46].

3. 1. 1. 6. Comparison between crystalline and amorphous powder

Table 3-5. Comparison two different powders [38, 40].

Crystalline Boron	Amorphous Boron
Steel gray or black color and very hard	Brown
Inert in nature	Relatively more reactive
Not attacked by air	Attacked by air
Not attacked by any oxidizing acid	Attacked by HNO3 and H2SO4

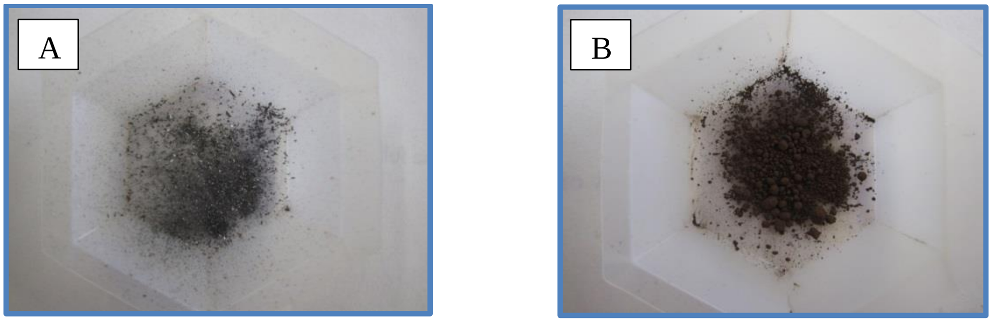

Figure 3-3. Crystalline boron powder (A) and amorphous boron powder (B).

As shown above table 3-5 and figure 3-3, crystalline and amorphous boron powders are shown different characteristics. The color of the crystalline boron powder is gray, while amorphous boron powder is brown. The crystalline boron powder has rough feel, but amorphous boron powder showed smooth texture.

However there was not any information about its difference in tribological performance. It is possible to determine which powder shows better results as lubricants' additive from this research.

3. 1. 2. Test specimen

For the galling tests, specimens should show sensitivity to the galling. In this research, "Inconel A 718," a nickel chromium material was used. This alloy is widely used in a variety of industries such as rockets, casings, aircrafts and engines since it has good properties: high tensile and fatigue strengths. The test specimen's detailed information is given in table 3-6 ~ 3-7.

Table 3-6. Elemental contents of the test specimen [51].

Element	Ni+Co	Cr	Fe	Nb+Ta	Mo	Ti	Al
Content (%)	50-55	17-21	17	4.75-5.5	2.8-3.3	0.65-1.15	0.2-0.8

Table 3-7. Properties of the specimen [51].

Density	8.19g/cm3
Melting point	1260~1336℃
Magnetic Permeability	1.0011 at room temperature
Specific Heat	435j/kg
Electrical Conductivity	Volumetric, 1.7% IACS at 21℃
Coefficient of Thermal Expansion	14.0µm/mK at 538℃ 15.8µm/mK at 871℃

3. 2. API RP 7A1 tests

In order to examine the boron powder's tribological performance, API RP 7A1 tests will be conducted in this study. The API RP 7A1 test is a small scale test procedure that was developed in the early 1990s. The test procedure has been conducted using shouldered fixtures with cylindrical specimen. The thread compounds are positioned between two surfaces and the generated film thickness is very thin [52]. As mentioned at the beginning of this chapter, two different greases were used as reference compounds: Calcium fluoride bolt lube standard formulation and the Super Lube grease. The characteristics of the test compounds are shown below table 3-8 ~ 3-9.

Table 3-8. Characteristics of the Calcium Fluoride bolt lube standard formulation [51].

Component	Wt (%)	Particle Size	Under 0.1mm
Lithium Grease	55 ± 1.0	Consistency	Worked penetration(60strokes): 310-340
Calcium fluoride superfine	35.0 ± 1.0	Thickener	Lithium 12-hydroxystearate: 5.5-7.2(%)
Calcium sulfate	8.0 ± 0.5	Base Oil	Petroleum/Non-synthetic
Vanlube 73	2.0 ± 0.5	Viscosity	@ 40℃ 115cSt minimum 170cSt maximum
Total	100		@ 100℃ 9.5cSt minimum 14.0cSt maximum

Table 3-9. Characteristics of the Super Lube® grease formulation [53].

Component	Wt (%)	Particle Size	Sub-micron
Polyalphaolefin	< 75	Consistency	Worked penetration(60strokes): 265-295
White mineral oil	< 25	Thickener	Fumed Silica (5%)
Fumed Silica	< 5	Base Oil	Polyalphaolefin(PAO)/synthetic
Polytetrafluoroethylene	< 4	Viscosity	@ 40℃ 75.5cst
Antioxidant	< 2		
Polyglycol	< 1		@ 100℃ 8cSt

3. 2. 1. Test machine

As shown in figure 3-4, the thread compound test machine is comprised of 6 parts: computer, control panel, motor / gear box, torque and rotation transducer, and cartridge assembly. The thread compound test machine is operated either manually, or automatically, by the control panel/computer. The option to control the test machine manually is used in cases where the machine is unresponsive to computer controls.

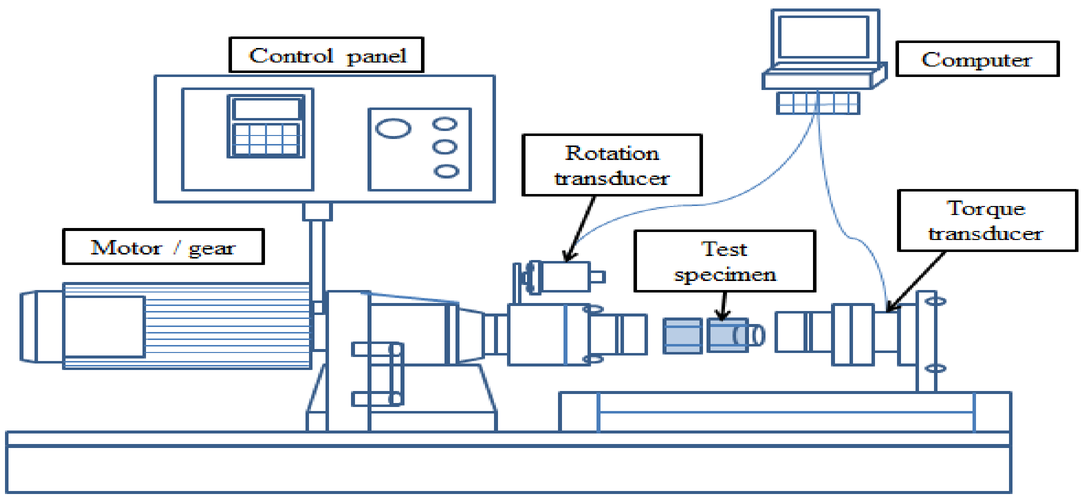

Figure 3-4. Diagram of API RP 7A1 test machine [51].

Operation instructions are delivered from the computer and it conducts, collecting and analyzing the gathered data. Motor/gear box serves to provide torque to the specimen with varying speeds between 1 and 5 RPM, and 3 RPM was used in this research. The torque transducer sends the output signal back to the computer, and the rotation transducer, as the name implies, provides information on the degree of the rotation of the specimen to the computer. The cartridge assembly consists of load cells and hex sockets. It applies a compressive load to the specimen located between the hex sockets.

3. 2. 2. Test procedure

Below are the three processes that ensure a thread compound's complete tests provide accurate results. Each process is composed of at least 5 up to 10 different tests.

1) Measuring the reference compound's frictional behavior
2) Measuring the test thread compound's frictional behavior
3) Repeat test for the reference compound's frictional behavior [51].

A thread compound's frictional performance can be obtained through processes using cylindrical specimens with compressive load cells. Detailed information of each test in every process will be described in the following paragraphs.

Calibrations must be carried out before the tests in order to ensure accurate data and make sure that the loads are not over a certain level in the load and torque cell. It should be noted that the torque variation must not exceed 14 N-m (10 ft-lb).

An appropriate amount of grease is applied to cover the surface of the prepared specimen and then mounted in the load cell. Measured data will be stored automatically by the computer with computerized equipment. Once the machine operates, all the data including torque, load, and the rotation of the specimen is recorded as the load reaches to 55,000 pounds. This process is called the make-up process.

After the make-up process is complete, the specimen will be loosened by the break-out process which has an opposite direction of torque. The completion of the make-up and break-out process is only one test which requires at least 5 to 10 rounds to obtaining accurate data.

These are the test procedures for a grease using an API RP 7A1 machine. It is possible to obtain a grease's friction factor which is a relative value of the grease's frictional performance with the reference compound. If the friction factor is over 1, the measured grease has higher frictional performance than the reference compound and vice versa.

3. 2. 3. Test result analysis

3. 2. 3. 1. Visual method

The test specimen should be cleaned with proper solvent after a test in each process. After that, the test specimen will be examined by naked eyes. If there were any traces of galling, the compound would not meet the requirements as a grease. Therefore, the test is completed at that moment and the compound will be condemned as a lubricant. If there is no signs of galling, then data analysis will be needed to compare the test thread compound to the reference compound.

3. 2. 3. 2. Data analysis

Lots of data will be recorded automatically in the computer that is connected to the machine. In order to analyze the data, data extracting will be needed. All data can be opened with Excel spreadsheet, then extract the specific range of make-up torque from 200 ft-lb to 300 ft-lb (271 N-m to 407 N-m) and rotation value being matched to the torque. In order for analyzing in this method, at least 20 pairs of values should be needed and it is possible to get the slope “m” whose value is the least square fit of a straight line of between torque and rotation. From this process, it is possible to get the friction factor which is a relative value indicating that the thread compound has better performance than the reference compound or not. It is because if the value is over 1 which means thread compound’s slope is higher than that of reference compound. The friction factor can be calculated by this simple formula as shown below [52].

$$\mathrm{FF} = \frac{2 \cdot S_2}{S_1 + S_3}$$

Where S_1 is the average slope of the first 8 runs of the reference compound.

S_2 is the average slope of the 8 runs of the test thread compound.

S_3 is the average slope of the second 8 runs of the reference compound.

3. 3. Tribometer experiments

A pin-on-disk tribometer (CSM Instrument) is used to measure the variation of coefficient of friction (COF). This tribometer is widely used in such as material, lubricants and self-lubricating systems. This is a direct measurement of the coefficient of friction and wear behavior with the desired speed by moving a flat disk.

3. 3. 1. Test preparation

The specimen used for the tribometer tests was the same test specimen used in API RP 7A1 tests. The specimen and the ball bearing were cleaned with acetone before each test. The specimen was grinded with 180, 400, 600, 800, 1200 grit sand paper in order to obtain a smooth surface texture.

The contact area of ball bearing on the specimen was too small compared to the boron particle's size. In order to compare boron powder's effect in lubricants, two flat surface rubbing each other were needed requiring the ball bearing to be grinded before each test for 2 hours to achieve flat surfaces. The generated flat area bearings are an elliptic shape 2 mm in diameter and 1.5 mm in diameter for the shorter side.

For the emulsion, the amount of components used in this research as follow: mineral oil (heavy) 75wt (%), 19.5wt (%) of water, 0.5wt (%) of emulsifier and 5wt (%) of amorphous boron powder.

3. 3. 2. Test procedure

A sample is positioned on the disk and the instrument can rotate, or reciprocate, the sample. As a result of the moving sample, frictional force will be generated between the sample and prove as shown in figure 3-5. During the tests, the values of the coefficient of friction are recorded precisely at a specified interval of time. The sample is the same as API test specimen and the reciprocate mode is selected to move the specimen with an amplitude of 10 mm. The applied scanning speed differed from 0.7 cm/s to 40 cm/s for the Stribeck curve analysis. There are three variables in the Stribeck curve: viscosity, rotation speed, bearing unit load. Rotation speed and bearing unit load can be simply controlled at each time. In order to acquire the viscosity, an AR-G2 rheometer was used.

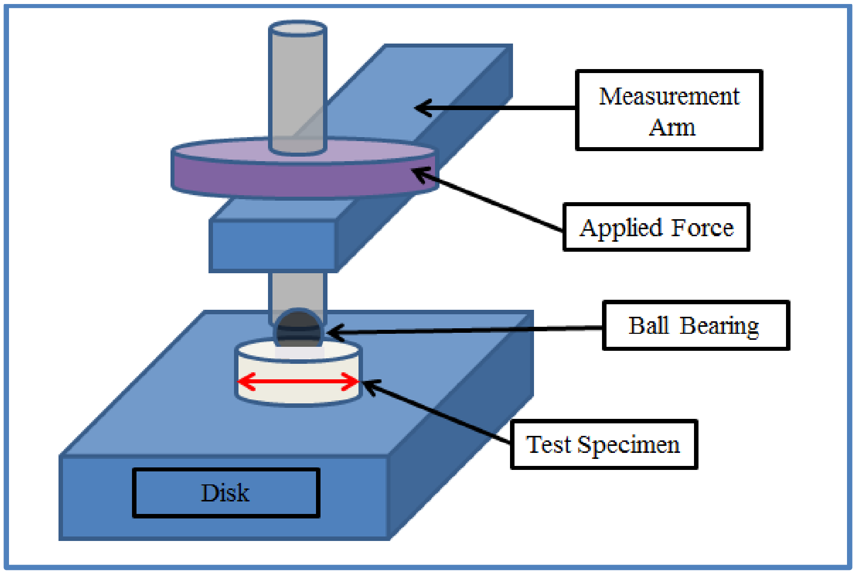

Figure 3-5. Diagram of pin-on-disk tests.

Another experiment was conducted for analyzing the COF variation along with over time. For this test, 2N of force was applied and the tests were last for 10 minutes. The other conditions were the same as Stribeck curve analysis tests.

3. 4. Characterization of the wear scar and component analysis

3. 4. 1. Surface analysis

A Keyence VHX-600K optical microscope was used for observing the wear scar after the Stribeck curve analysis tests. This provided the basic property of the wear scar, but it was not enough to characterize it, because it has a low resolution and does not provide the information of the wear depth. For this reason, Zygo newview 600s was used for three-dimentional characterization of the wear scar. Zygo test machine uses interferometry to measure the surface roughness and provides general information about the wear scar including wear depth and 3D images as shown in figure 3-6. There are three objectives: 10x, 20x, 50x with the test machine, and10x objective was used in this research.

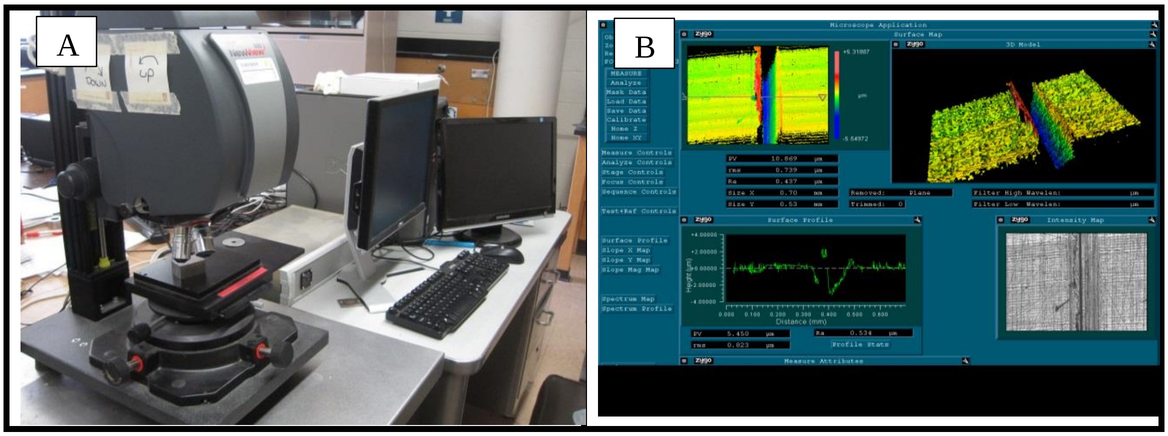

Figure 3-6. Zygo newview 600s test machine A, wear scar profile B.

In addition, a scanning electron microscope was used to obtain the more detailed information on the wear scar. The scanning electron microscope has higher resolution compared to the optical microscope that provides only restricted information about the wear scar.

3. 4. 2. Raman spectroscopy

Raman spectroscopy was used for obtaining the information on the structure of the molecules and powders used in this research. It uses inelastic scattering of a photon as shown in figure 3-7. The inelastic scattering of a photon was first observed by C. V. Raman in 1928 [54]. Usually a re-emitted photon has the same energy as the original photon which is called Rayleigh scattering, but Raman found that photon energy is changed during the raman scattering, because the initial photon interacts with the surrounding materials.

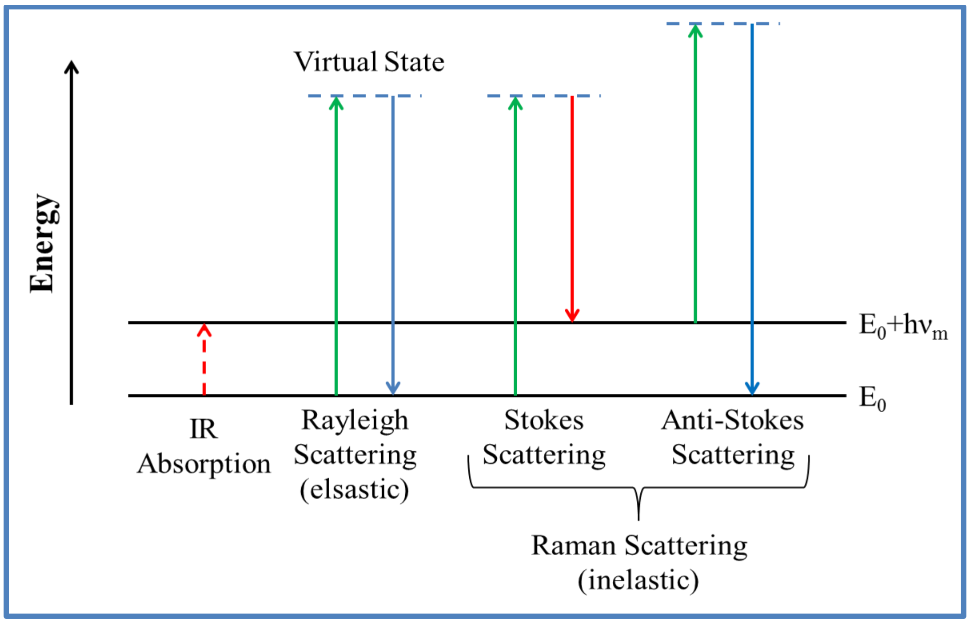

Figure 3-7. Different scheme for photon scattering.

Raman spectroscopy is a very prevailing device in analyzing a molecular structure of any kind of material: gas, liquid, powder or any solid materials. For this research 532nm of wavelength was used, and the laser power was 0.3 watt.

CHAPTER IV

EFFECTS OF BORON ON LUBRICATING PERFORMANCE IN GREASE

4. 1. Galling experiments

4. 1. 1. Visual examination

After each test, the specimen should be examined by the naked eye. If there was any trace of galling or scratches, the tests would be stopped from that point. The presence of galling means that the crystalline boron powder failed to lubricate, as shown in figure 4-1. Figure 4-1A shows the specimen before the tests, and figure 4-1 B is the after picture. There was a presence of numerous scratches and galling traces shown in figures B and C. The figure 4-1 C is the magnified imagine of 4-1 B, where circled in red after conducting a test using crystalline boron powder as an additive for the thread compound. However there was no galling in amorphous boron powder mixed grease tests.

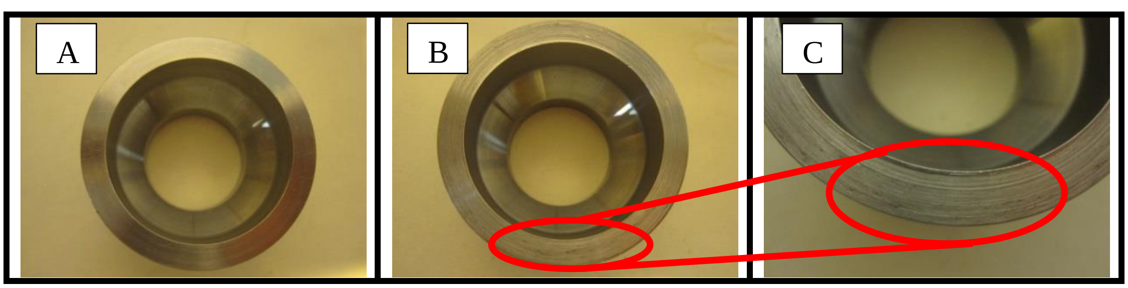

Figure 4-1. Examination of specimen surface by naked eyes.

According to Figure 4-1, it is believed that the crystalline boron powder caused abrasive wear. This is proved by the Vickers hardness results. The Vickers hardness of crystalline boron is 42 ~ 58 Gpa and the Vickers hardness of α-B_2O_3 (a low-pressure phase) is not known, but β-B_2O_3 (a high-pressure phase) is about 16 Gpa while amorphous boron oxide's Vickers hardness is only 1.5 Gpa. It is clear that a hard and abrasive material is not suitable as a lubricant additive.

4. 1. 2. Evaluation of friction factor for thread compounds

Tribological performance of test compounds was evaluated in terms of friction factor. Boron-added calcium fluoride reference compound and Super Lube, a commercial grease were used in this research.

First of all, non-oxidized boron powder was used as an additive. As mentioned in Chapter III, there were three steps, each step consisted of 8 different tests as shown in table 4-1.

Table 4-1a. Results for the first 8 runs of calcium fluoride reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	464.5	322.4	69.41	300.96	197.6	173	3.89	61634	270.3
2	459.6	306.9	66.78	300.39	195.8	176	3.72	61796	265.7
3	460.8	304.9	66.18	300	197.9	173	3.78	62447	280.1
4	450.1	302.4	67.2	279.4	199.9	174	3.81	61943	292.6
5	451.1	300.4	66.59	306.4	200	175	3.79	62365.8	235.1
6	452.9	312.4	68.98	305.5	198.7	173	3.99	62593.5	232.3
7	447.2	299	66.86	304.7	199.3	178	3.71	62691	232.2
8	450.1	305.1	67.78	301.7	195	185	3.82	62045.5	235.7
Average	454.5	306.7	67.5	299.9	198.0	175.9	3.8	62189.5	255.5

Table 4-1b. Results for the 8 runs of 5wt (%) amorphous boron added reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	440.8	292.1	66.3	306.3	193.7	187	3.68	57215.3	303.4
2	445	298	66.98	307.1	198.1	187	3.56	57819	306.1
3	441	294.9	66.9	308.1	197.3	189	3.54	57476	245.1
4	439.9	290.3	66	302.5	194.1	187	3.62	57655.8	308.6
5	444.1	302.1	68	301.6	195.8	187	3.55	57933.1	303.4
6	473.9	345	73.9	303.7	195.2	176	3.85	55274.1	322.3
7	470.7	345.9	73.5	302.9	196.6	187	3.68	55665.6	306.5
8	469.8	338.5	72.1	309	193.9	187	3.77	55518.8	242
Average	453.2	313.4	69.2	305.2	195.6	185.9	3.7	56819.7	292.2

Table 4-1c. Results for the second 8 runs of calcium fluoride reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	440.1	300.5	68.3	308.1	198	173	4.05	62577.3	238
2	432	396.9	68.7	300.2	200	161	3.93	62496	236.3
3	436.8	307	70.3	302.8	193.8	172	3.97	62463.4	240.5
4	438.4	298.6	68.1	302.2	196	173	3.86	62154.4	235.8
5	436.6	297.3	68.1	302.3	193.9	186	3.8	62300.7	264.7
6	434.9	285.1	65.6	307.3	198.3	187	3.73	62186.9	233.6
7	437.2	289.5	66.2	307.4	197.5	187	3.69	62479.7	237.9
8	437.5	291.3	66.6	300.7	200.3	159	3.88	62788.7	299.1
Average	436.7	308.3	67.7	303.9	197.2	174.8	3.9	62430.9	248.2

Here the Maximum Make-up torque means recorded maximum torque with applying force, and maximum break-out torque is the maximum torque when the specimen was loosened in the opposite direction. The upper torque curve fit and lower torque fit indicate that the highest and the lowest torque value ranging of torque from 200 ft-lb to 300 ft-lbs as mentioned in chapter III. Number of data points for curve fit is the pairs of number in the torque from 200 ft-lb to 300 ft-lbs and at least 20 pairs are needed to analyze the friction factor. Slope of line is the least square fit of a straight line between torque and rotation degree of the specimen. Finally maximum load means the highest load value that was applied in the each tests, usually this is corresponding with the greases performance.

From these results, it is obvious that only amorphous boron powder is not good as an additive in grease. The average slope of the first 8 runs of calcium fluoride was 3.8, and the average slope of the second 8 runs of reference compound was 3.9. The slope of the reference compound with amorphous boron powder was only 3.7. The calculated friction factor was 0.95, which indicated that the boron reduced the reference compound's frictional performance by 5%. This is because the slope of line indicated that how the specimen has been turned by certain torque. In other words, if a grease's performance is improved, a higher torque is needed to turn the specimen to the same degree.

In table 4-2, the compound with 5wt (%) oxidized amorphous boron showed better results. For this set of tests, amorphous boron powder was oxidized in an electric furnace at 70℃ for 4 hours. The amorphous boron powder is very sensitive and can be oxidized under normal atmospheric circumstances. The results showed an improved friction factor of 1.04, which indicated the oxidized amorphous boron powder increased the grease's performance about 4% as shown in table 4-2.

Table 4-2a. Results for the first 8 runs of super lube reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	509	406.9	79.9	307.9	196.1	170	4.08	51484.5	280.9
2	509.6	379.9	74.6	301.2	197.8	169	4.12	51630.8	244.8
3	507.4	355.1	70	305.9	199.7	173	3.98	54736.3	249.2
4	461.1	310.3	67.3	303.1	202.4	174	3.89	56687.4	244.8
5	480.7	330.8	68.8	301	202.2	175	3.79	56215.9	277.8
6	500.2	375.9	75.2	301.2	202.1	160	4.03	54508.7	284
7	456.9	303.1	66.3	304.2	201.3	188	3.54	56719.9	247.2
8	491.2	375.5	76.4	300.1	198.9	172	3.84	55446.1	243.2
Average	489.5	354.7	72.3	303.1	200.1	172.6	3.909	54678.7	259.0

Table 4-2b. Results for the 5wt(%) oxidized amorphous boron added super lube compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	498.5	363.2	72.9	300.2	200.7	160	4.05	52906	238.5
2	507.9	386.9	76.2	301.8	200	166	4	51764.5	241.8
3	499	356.4	71.4	300.2	199.2	164	4.05	48273	236.8
4	495.7	378.8	76.4	300.9	198.9	161	4.06	53349	240.8
5	501.1	383.5	76.5	306.4	197.2	180	3.87	51674.5	237.7
6	499.9	379.1	75.8	301	199	166	3.85	52650	192.8
7	491.8	372.8	75.8	301.6	197.9	165	3.98	52910	232.3
8	496.5	378.7	76.3	300.1	199.5	166	3.88	54860.8	243.1
Average	498.8	374.9	75.2	301.5	199.1	166.0	3.968	52298.5	233.0

Table 4-2c. Results for the second 8 runs of super lube reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	512.2	388	75.8	300.3	200.7	160	4.11	52174.9	239.6
2	487.3	372.4	76.4	302.3	198.8	186	3.83	56324	245.9
3	504.2	380.3	75.4	303	200.3	174	3.95	56010.1	181
4	452.6	356.7	78.8	306.4	200.1	188	3.69	56887.8	183.7
5	444.8	357.6	80.4	302.3	197.6	191	3.52	56692.7	238.8
6	435.6	304.8	70	304.7	197.6	197	3.52	57261.6	239.1
7	446	354.2	79.4	303.1	196.1	188	3.68	57196.6	238.6
8	410.3	286	69.7	304.4	200.7	189	3.64	57716.7	242.8
Average	461.6	350.0	75.7	303.3	199.0	184.1	3.743	56283.1	226.2

In order to examine the boron powder's concentration effect, greases with different amount of boron powder were tested as shown in Tables 4-3 and 4-4. Table 4-3 shows that the friction factor was 0.99 which indicates that only 1 wt (%) addition of boron reduced a grease's frictional behavior.

Table 4-3a. Summary of the data collected for the first 8 runs using the reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	455.4	314	69	306	198.4	149	4.64	56901.7	306.7
2	456.7	324	70.9	303.4	204	146	4.53	56901.7	220.3
3	456.9	316.7	69.3	302.9	200.9	144	4.63	56918	238.3
4	453.8	314.3	69.3	307.8	203	146	4.7	56251.3	246.7
5	453.1	317.2	70	300.2	198.8	154	4.47	57031.8	296.4
6	445.2	305.2	68.6	301.4	201.5	150	4.39	56787.9	255.6
7	450.8	315.5	70	300.7	196.9	149	4.59	57096.8	296.6
8	450.2	312.4	69.4	302.9	199	148	4.6	57161.9	303.8
Average	452.8	314.9	69.6	303.2	200.3	148.3	4.569	56881.4	270.6

Table 4-3b. Summary of the data for the 8 runs using the boron 1% mixed reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	446.6	307.7	68.9	302.1	197.8	150	4.6	56771.6	236.1
2	457.3	316.6	69.2	306.1	200	150	4.65	57373.2	300.7
3	452.7	311.5	68.8	302.8	197.9	159	4.5	57048	240.7
4	447.7	313.6	70.1	306.7	200.1	150	4.53	56869.2	296.6
5	447.6	315.6	70.5	302.5	197.1	150	4.54	57178.1	292.2
6	446.9	312.3	69.9	300.1	201.1	148	4.59	56999.3	301
7	453.8	316.4	69.7	302.8	198.8	159	4.49	57194.4	286.7
8	446.8	306.7	68.6	302.1	201.6	150	4.47	56739.1	295.6
Average	449.9	312.6	69.5	303.2	199.3	152.0	4.546	57021.6	281.2

Table 4-3c. Summary of the data collected for the second 8 runs using reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	455.4	314	69	306	198	149	4.64	56901.7	306.7
2	429.2	313.2	73	301.1	196.7	150	4.71	56953.8	298.4
3	434.6	309.3	71.2	302.9	196.8	149	4.69	57230.1	300.7
4	434.9	310.7	71.4	300	198.1	149	4.61	57035	235.8
5	436.1	312.7	71.7	300.3	198.8	157	4.65	57197.6	227.8
6	436.4	309.9	71	300.4	199.6	144	4.72	57311.3	289.6
7	430.1	310.2	72.1	302.4	201.9	146	4.63	56956.8	292.7
8	434.6	304.3	70	304.9	198.2	158	4.64	56970	238.2
Average	436.4	310.5	71.2	302.3	198.5	150.3	4.661	57069.5	273.7

Table 4-4 introduced the test results of 2wt (%) added compound's frictional behavior. According to the results, the calculated friction factor was 1.0, which implied that 2wt (%) boron added grease showed slightly better results compared to the 1wt (%) added compound.

Table 4-4a. Summary of the data collected for the first 8 runs using the NCS-30 compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	442.9	316.2	71.4	300.5	197.3	177	3.86	56736.5	344
2	438.9	311.9	71.1	302.1	200.5	173	3.94	56834.2	231.7
3	431.7	304.2	70.5	304	199.8	186	3.83	57631.5	299.1
4	429.8	306.6	71.3	302	197.1	187	3.67	57078.2	230.5
5	443.7	312.8	70.5	302	201	173	3.96	57360.7	237.4
6	431.1	310.6	72	306.4	197	186	3.8	57165.6	227.4
7	433.5	306.2	70.6	300.3	199.5	185	3.73	57458.3	229.8
8	437.7	307.2	70.2	301.5	196.6	186	3.87	57507.1	225.4
Average	436.2	309.5	71.0	302.4	198.6	181.6	3.833	57221.5	253.2

Table 4-4b. Summary of the data collected for the 8 runs using the boron 2% mixed NCS-30.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	421.5	302.6	71.8	301.7	198.1	172	3.99	57264.6	232.4
2	425.9	304.9	71.6	300.3	196	170	3.91	57492.2	225.5
3	422.4	296.6	70.2	301.2	199	174	3.84	57768.6	238
4	415.7	290.1	69.8	303.4	199.7	174	3.86	57410.9	233.8
5	408	288.9	70.8	300.8	196	182	3.89	57232.1	225.7
6	409.1	289.4	70.7	301.1	201.1	148	3.86	56999.3	301
7	453.8	316.4	69.7	302.8	198.4	178	3.86	57362.1	232.3
8	411.9	289	70.2	303.8	198.1	177	3.86	57541	246.6
Average	421.0	297.2	70.6	301.9	198.3	171.9	3.884	57383.9	241.9

Table 4-4c. Summary of the data collected for the second 8 runs using NCS-30 compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	410.7	295.2	71.9	300.2	196.8	180	3.93	57524.7	234.6
2	414.8	291	70.1	305.3	202.5	174	3.91	58110	234.9
3	409.7	290.6	70.9	301.1	199.4	164	3.98	57849.9	229.8
4	409.4	280.6	68.6	301.8	200.2	173	3.84	57784.9	240.9
5	410.7	281.8	68.6	300.7	199.6	164	4.05	577.03.6	231.7
6	409	284.3	69.5	301.1	198.8	173	3.93	57589.8	237.5
7	405.8	280.3	69.1	302	198.4	177	3.76	57573.5	228.6
8	412.2	290.3	70.4	301.2	201.1	174	3.86	57931.2	228.1
Average	410.3	286.8	69.9	301.7	199.6	172.4	3.908	57766.3	233.3

According to these data, a compound with 5wt (%) oxidized boron showed the best results, and the tribological performance improved as the amount of boron increased. Several emulsion added grease were also tested to determine the emulsion's effect on the greases' performance under extreme pressure as shown in table 4-5~4-6.

Table 4-5a. Summary of the data collected for the first 8 runs using the NCS-30 reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	417	274.1	65.7	300.1	200.7	201	3.35	57765	234.8
2	414.7	272.2	65.6	301.7	200.3	194	3.48	57813.8	234.8
3	405.2	266.1	65.7	300.6	197.6	205	3.37	57423.3	228
4	408.2	266.8	65.4	306.3	200.9	203	3.36	57488.4	230.5
5	407.9	274.8	67.4	306.3	200	202	3.38	57553.5	234.2
6	412.7	277.1	67.1	303.6	197.7	201	3.39	58741.5	227.4
7	401.9	261.6	65.1	307.1	199	202	3.49	57852.4	229.9
8	396.8	260.3	65.6	304.3	199.1	202	3.37	57478.4	227.8
Average	408.1	269.1	66.0	303.8	199.4	201.3	3.399	57764.5	230.9

Table 4-5b. Summary of the data collected for the 8 runs using the boron 1% emulsion.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	393.5	258.8	65.8	304.6	197	202	3.46	57522.1	226.7
2	402.6	264.6	65.7	302	195.9	215	3.28	57392.1	231.1
3	403.4	266.6	66.1	300.9	200.9	198	3.38	58026.1	237.8
4	409	272.1	66.5	305.9	197.3	202	3.43	57879.7	234
5	396.9	261.9	66	303.7	196.1	215	3.29	57392.1	288.9
6	413.2	279	67.5	302	197.2	201	3.4	57392.1	292.6
7	403.4	265.9	66.1	305	198.3	202	3.44	57473.3	231.9
8	423.4	280.7	66.3	302.4	200.8	203	3.31	57489.6	296.3
Average	405.7	268.7	66.3	303.3	197.9	204.8	3.374	57570.9	254.9

Table 4-5c. Summary of the data collected for the second 8 runs using NCS-30 reference compound.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	393.5	258.8	65.8	304.6	197	202	3.46	57522.1	226.7
2	402.6	264.6	65.7	302	195.9	215	3.28	57392.1	231.1
3	403.4	266.6	66.1	300.9	200.9	198	3.38	58026.1	237.8
4	409	272.1	66.5	305.9	197.3	202	3.43	57879.7	234
5	396.9	261.9	66	303.7	196.1	215	3.29	57392.1	288.9
6	413.2	279	67.5	302	197.2	201	3.4	57392.1	292.6
7	403.4	265.9	66.1	305	198.3	202	3.44	57473.3	231.9
8	423.4	280.7	66.3	302.4	200.8	203	3.31	57489.6	296.3
Average	405.7	268.7	66.3	303.3	197.9	204.8	3.374	57570.9	254.9

Table 4-6a. Summary of the data collected for the first 8 runs using the NCS-30 reference grease.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	367.2	236.3	63.4	304.9	200.7	216	3.21	57735.7	290.9
2	374	240.3	64.3	301.4	196.8	205	3.33	58028.8	234.1
3	374	244.7	65.4	304.2	199.6	215	3.27	58826.8	290.9
4	313.2	196.1	62.6	300.6	197.4	220	3.05	59186.4	264.9
5	370.1	241	65.1	304.9	198.5	215	3.2	58255.3	264
6	363.7	235.5	64.8	302.4	196.1	228	3.16	57832	295.7
7	365.9	236.9	64.7	302.6	197.7	201	3.37	58239	289.4
8	372.9	244.8	65.6	303.1	195.4	215	3.21	58662.3	295.7
Average	362.6	234.5	64.5	303.0	197.8	214.4	3.225	58345.8	278.2

Table 4-6b. Summary of the data collected for the 8 runs using the boron 5% emulsion.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	378.4	252.7	66.8	301.4	197	212	3.29	58279.8	292.5
2	391.2	260.9	66.7	301.5	199.5	213	3.27	58279.8	291.4
3	396.6	260.2	65.6	300.1	198.5	202	3.3	58165.8	292
4	407	273	67.1	300.8	197.7	205	3.39	58035.4	346.9
5	405.6	270.9	66.8	305.2	196.3	201	3.6	57742.2	285.1
6	403.2	275.7	68.4	302.5	200.7	188	3.54	57465.2	289.3
7	401.6	272.3	67.8	305.9	201.8	203	3.43	58182	349.3
8	374	255.1	68.2	304.1	195.7	215	3.32	58605.6	289.3
Average	394.7	265.1	67.2	302.7	198.4	204.9	3.393	58094.5	304.5

Table 4-6c. Summary of the data collected for the second 8 runs using NCS-30 reference grease.

Run No.	Max MU Torque [ft-lbs]	Max BO Torque [ft-lbs]	BO to MU %	Upper Torque Curve Fit [ft-lbs]	Lower Torque Curve Fit [ft-lbs]	No. data points for curve fit	Slope of Line [ft-lbs/deg]	Max Load [lbf]	Rotation from Ref [deg]
1	384.6	266.7	69.3	305.5	197.9	201	3.54	57579.3	346.9
2	381.6	259.1	67.9	300.9	198	198	3.43	58016.1	291.1
3	386.2	258.5	66.9	301.9	199.7	196	3.53	58064.9	288.5
4	380.5	253	66.5	300.9	200.2	210	3.25	58146.3	289.8
5	381	255.8	67.1	300.8	199.7	193	3.35	58748.4	287.6
6	367.5	241.4	65.7	301.1	2008	202	3.35	58748.4	236.1
7	358.4	239.5	66.8	301.4	200.6	201	3.32	57902.2	230.8
8	384.8	254.3	66.1	301.6	200.3	188	3.54	58357.9	290.4
Average	378.1	253.5	67.0	301.8	425.6	198.6	3.414	58195.4	282.7

As shown in tables 4-5~4-6, the 1wt (%) boron added emulsion showed 0.99 of friction factor, which implies that the 1wt (%) emulsion did not have any effect on the reference compound. Furthermore, the 5wt (%) boron added emulsion showed only a 2% improvement. From these results, it can be concluded that emulsion did not have a great impact on grease's tribological performance under high pressure.

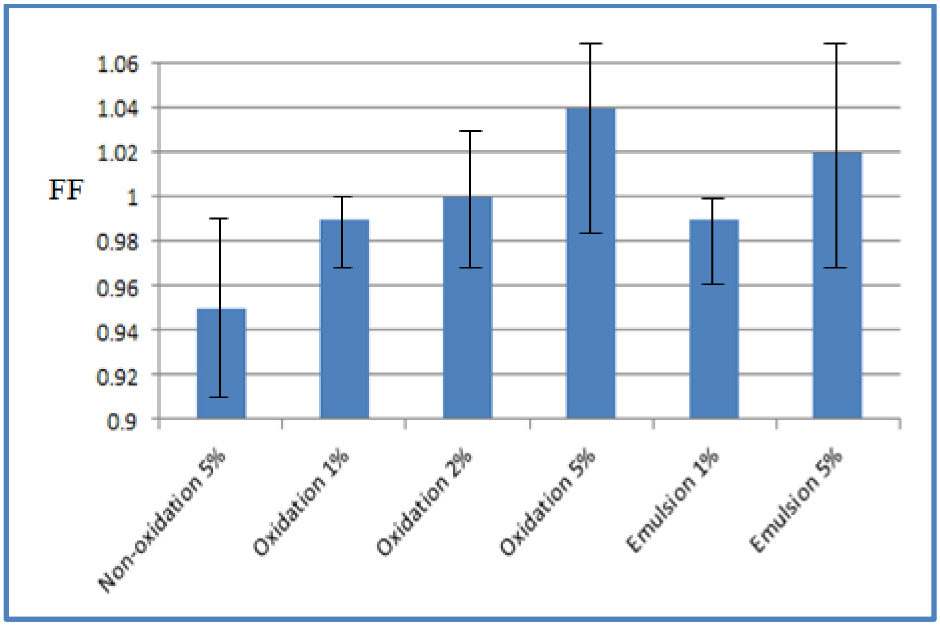

Figure 4-2. Obtained friction factor from API RP 7A1 tests.

Figure 4-2 is the overall results of calculated friction factor showing clear conclusions. The friction factor was increased with increasing the oxidized boron quantity up to 5wt (%).

It is possible to conclude these estimations from the API RP 7A1 tests:

1) Increasing boron contents increased the frictional performance up to 5wt (%).
2) Oxidation had a critical role to the boron powder showing better friction factor.

3) Emulsion did not show as the same lubrication properties as oxidized boron powder under high load experiments.

According to the results, oxidized boron added grease showed better friction factor than non-oxidized boron added grease. It is believed that when boron powder is oxidized, the structural properties would be changed to 2D boroxyl ring and planar BO_3 configurations. As mentioned in the chapter III, this plane structure affected to the grease's frictional behavior. For example, plane structure makes planar contact upon loading, while sphere structure makes point contact to the surface under the load as shown in figure 4-3 [55]. This difference makes the gap of the results. Because, when the load was applied to the specimen, the planar structure of the oxidized boron powder distributed the load, thus large power would be needed to turn the specimen at the same degree with the reference grease used results. Therefore, the calculated friction factor was over 1 in the case of oxidized boron added grease, since the friction factor was the least square fit of a straight line between applied torque and rotation degree of the specimen.

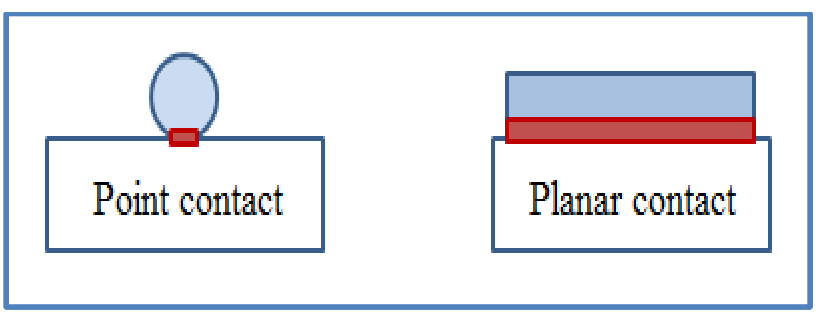

Figure 4-3. Examples of point contact and planar contact [55].

CHAPTER V

EFFECTS OF BORON ON OIL-BASED LUBRICANTS

5. 1. Effects of amount of boron in mineral oil

The different amounts of boron powder were added to the emulsion in order to examine its effects on lubricant. Figure 5-1 shows that the boron-added emulsion showed lower coefficient of friction compared to the reference mineral oil. In all cases, the coefficient of friction was fluctuated for 2 minutes since the beginning, and it became stabilized after 2 minutes till the end of the tests. According to Figure 5-1, 1% and 2% of boron powder showed the lowest coefficient of friction, while 5% boron added emulsion showed the highest among the boron added emulsion.

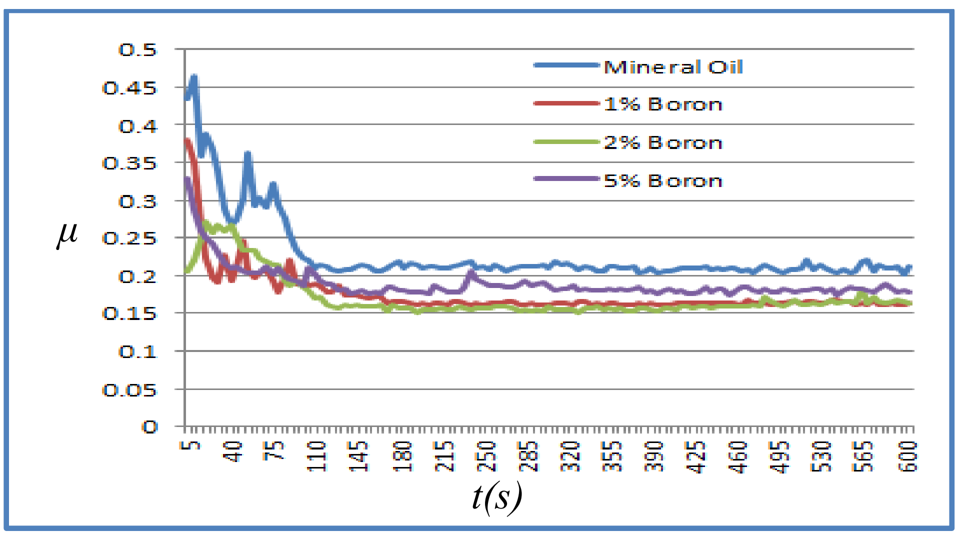

Figure 5-1. Tribometer test result for different amount of boron powder in emulsion.

5. 2. Stribeck curve analysis

There are three variables in the Stribeck curve: viscosity, rotation speed, and applied load. The applied rotational linear speed varied from 0.7cm/s to 40cm/s, and 2N of the applying load was constant for the Stribeck curve analysis. Figure 5-2 contains the test results without the emulsion technique. The oxidized amorphous boron powder was mixed in mineral oil. Results indicated that boron-added mineral oil showed a higher COF than the mineral oil alone. This is because the boron particles were agglomerated after mixing as mentioned in the experimental detail part in chapter III. Consequently, the boron powder was not spread on the specimen, and this reduced the frictional performance of the mineral oil.

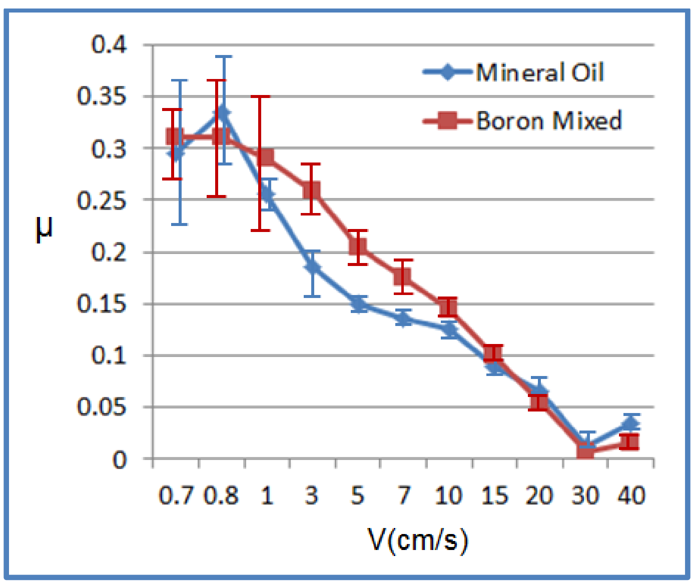

Figure 5-2. Tribometer test result for boron added mineral oil.

Lastly, the viscosity of the different compounds was measured by the AR-G2 rheometer as shown in figure 5-3. These values were angular velocities, so it should be transformed to tangential velocities to get the corresponding viscosities to the tribometer tests' speed.

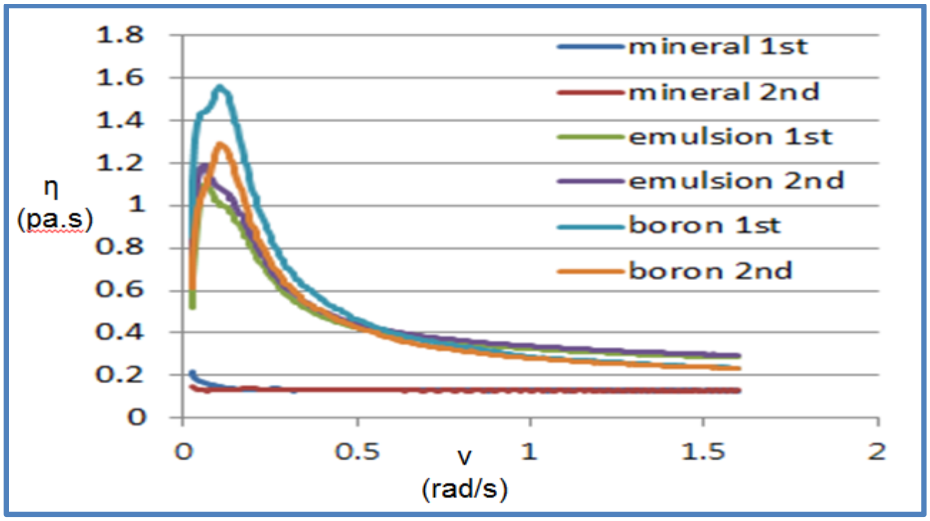

Figure 5-3. Viscosity variation with applied speed.

There were restrictions to get all the viscosity values with respect to the applied speed, because the maximum measured angular velocity was less than 2(rad/s), which is corresponding to only 2.5cm/s in the tribometer speed. Therefore, other viscosity values whose speeds were over 3cm/s in the tribometer tests were estimated from equations calculated from trend lines in the Microsoft Excel program.

After obtaining each viscosity value, it is possible to draw Stribeck Curve as shown in figure 5-4.

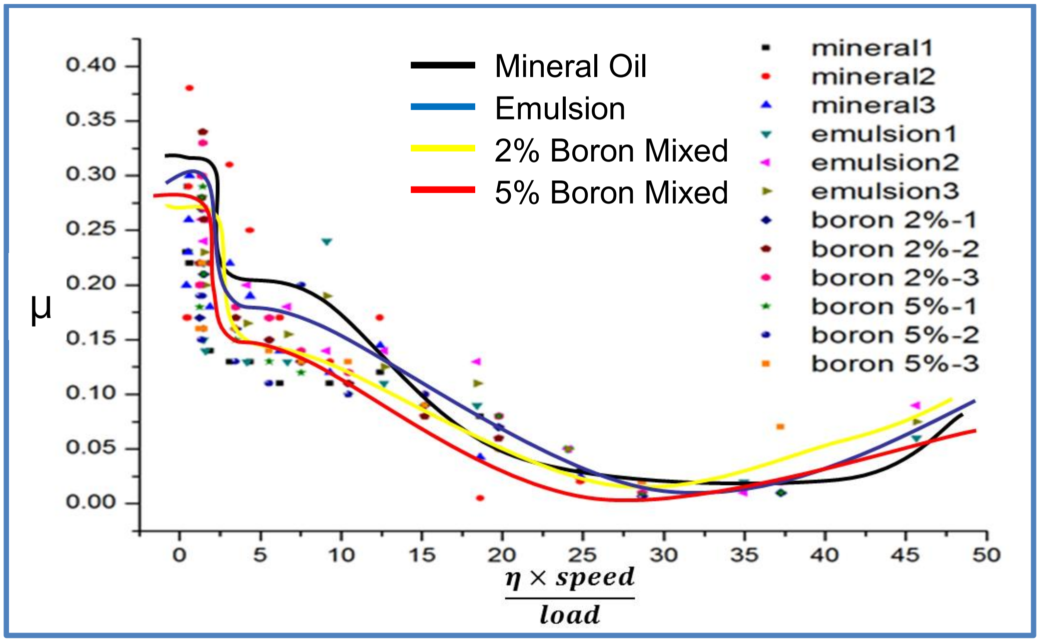

Figure 5-4. Stribeck curve analysis.

From these results, it is obvious that the boron added emulsion showed a lower Stribeck curve specifically under the boundary and the mixed lubrication regime than the other two compounds: just emulsion and mineral oil.

5. 3. Various surface observation analysis

The optical microscope, SEM and zygo newview 600s devices were used for observing the surface of the specimen in order for analyzing the wear scar.

5. 3. 1. Optical microscope

Figure 5-5 shows the wear scar observation after the stribeck curve analysis by VHS-600K optical microscope with 200 magnification. The results are somewhat controversial. Figure A indicates the wear scar of mineral oil, figure B is the wear scar of mineral oil and water emulsion (O/W), and figure C is the wear scar of 5wt (%) of boron added emulsion. In the case of mineral oil and just emulsion, the wear scar was 200 μm and 100 μm respectively. The boron added emulsion showed a wear scar almost 5 times wider than just emulsion. From these results, boron added emulsion showed the worse result than other two tests. Therefore, further study was needed to examine the wear scar precisely.

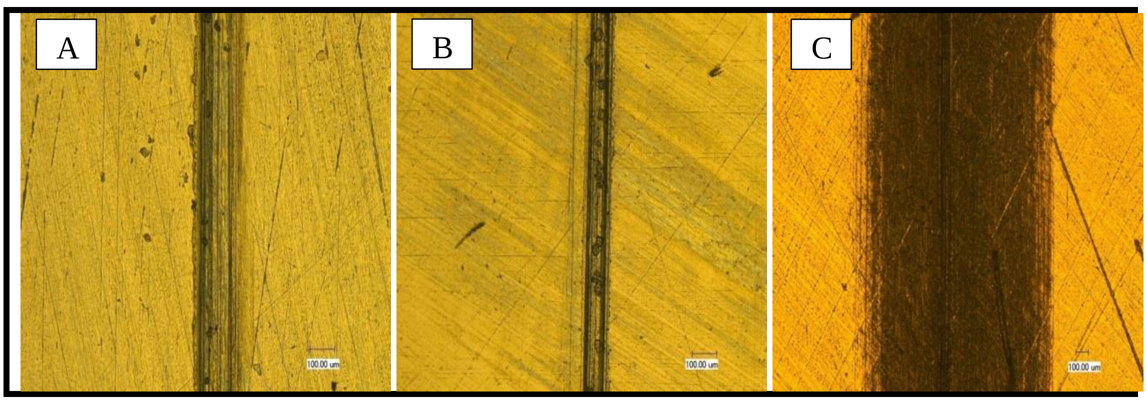

Figure 5-5. Wear scar observation by VHS-600K optical microscope with magnification of 200.

5. 3. 2. Zygo newview 600s

This device examined the wear scar in three dimensional characteristics. Therefore, it is possible to obtain wear rate of the wear scar from the observation. Figure 5-6 shows the test results. Figure A is the wear scar of just the mineral oil, figure B is the wear scar of just the emulsion, and figure C is the boron added emulsion wear scar. The results show clear conclusion that the mineral oil and the just emulsion test results exhibited about 4.5μm, 6μm of wear depth respectively, while the boron added emulsion had only under 1μm of wear depth. These results indicated that boron affected the critical role between two metal surfaces in terms of wear scar formation.

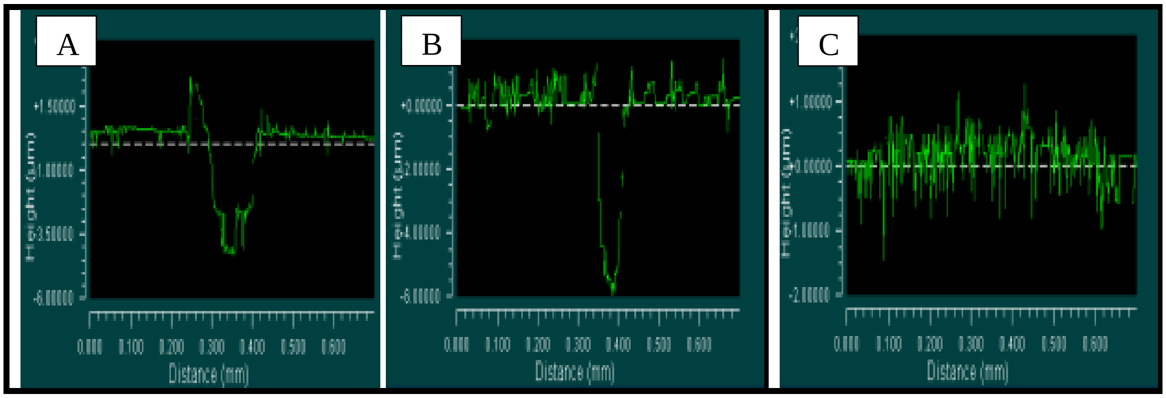

Figure 5-6. Wear scar observation by ZYGO newview 600s.

Wear rate calculation was obtained from this simple formula.

$$\mathrm{K} = \frac{V}{Fs}$$

Where K, V, F, s indicate specific wear rate, wear volume, applied force and distance of sliding respectively. The calculated wear rates are shown in figure 5-7.

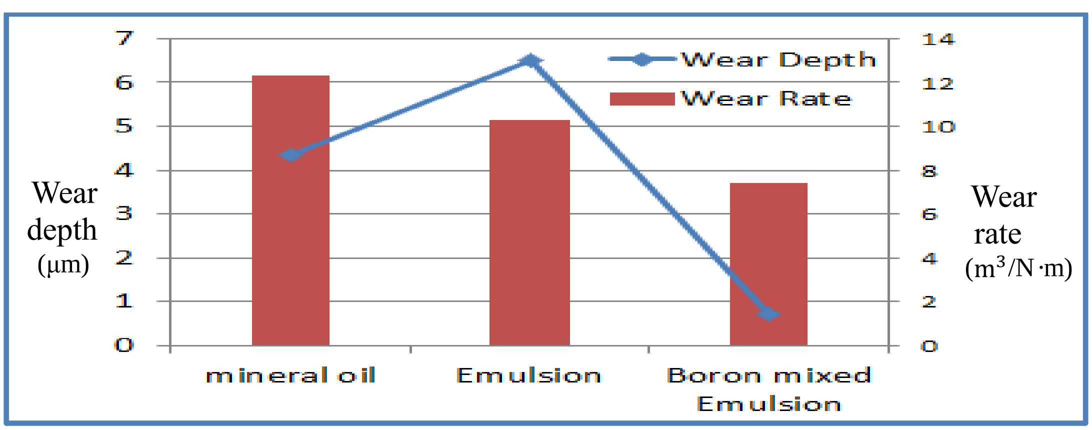

Figure 5-7. Wear depth and calculated wear rate.

As shown in figure 5-7, mineral oil showed the highest wear rate. Even though just emulsion had the deepest wear depth, the wear rate was lower than that of mineral oil. It is because the emulsion showed the narrowest wear scar. As expected from the figure 5-6, 5wt (%) boron added emulsion showed the lowest wear rate. The calculated wear rate of boron mixed emulsion was 40% less than just mineral oil test results. From these wear rate analyses, the boron added emulsion showed great tribological properties on the frictional surface.

5. 3. 3. Scanning electron microscope analysis

It was impossible to analyze the wear scar by optical microscope, since the wear scar was dark surface, and the resolution of the optical microscope was not enough to see the wear surfaces. Using SEM is an alternative way to acquire the detailed information of the surface topography. Because it has high resolution, and it can detect any kind of surface defects regardless of surface color by using electron beams. In that aspect, SEM is a useful device to get the wear surface topography for this research. Figure 5-8 is the SEM test results. It provided clear information about the wear surface. It was easy to determine the difference of the wear scar between the mineral oil and the boron added emulsion. Figure A is the wear scar of the mineral oil, figure B is the wear scar of the just emulsion, and figure C is the boron added emulsion wear scar after the Stribeck curve tests.

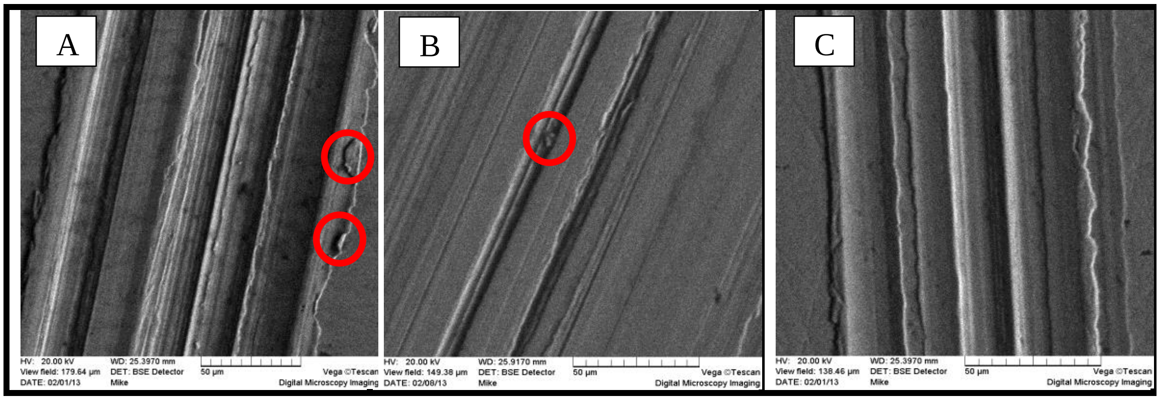

Figure 5-8. Wear scar observation by SEM.

As shown figure A, there were a lot of scratches in the center of the wear scar and the two red circles are indicating surface deformations that were caused from severe abrasive wear. Figure B is the just emulsion test result that shows there is similar deformation to the Figure A in the red circle. Furthermore, the side line of the wear scar is more deformed than the boron added emulsion test result (figure C). Figure C is the boron added emulsion test result showing that the center of the wear scar is relatively smooth and gentle.

According to the SEM test picture, it was possible to conclude that boron added lubricant showed less abrasive wear on the frictional surface than the other two cases. It is evident that oil film can be easily broken, when two metal surfaces are rubbing each other especially in low speed, but when there is a boron powder added as an additive, it can reduce the metal to metal contact area and reduce abrasive wear between two metal surfaces. Even though the wear scar is wider, the wear scar and wear depth is much less than that of mineral oil and just emulsion.

5. 4. Raman spectroscopy results

Raman spectroscopy is the way to examine the chemical structure of a material. It was used for obtaining the information of whether the boron powder's chemical structure was changed or not in this experiment as shown in figure 5-9. Figure A is the just amorphous boron powder test result, figure B is the oxidized boron powder reacted with water test result and figure C is the enlarged figure of the red box in figure B.

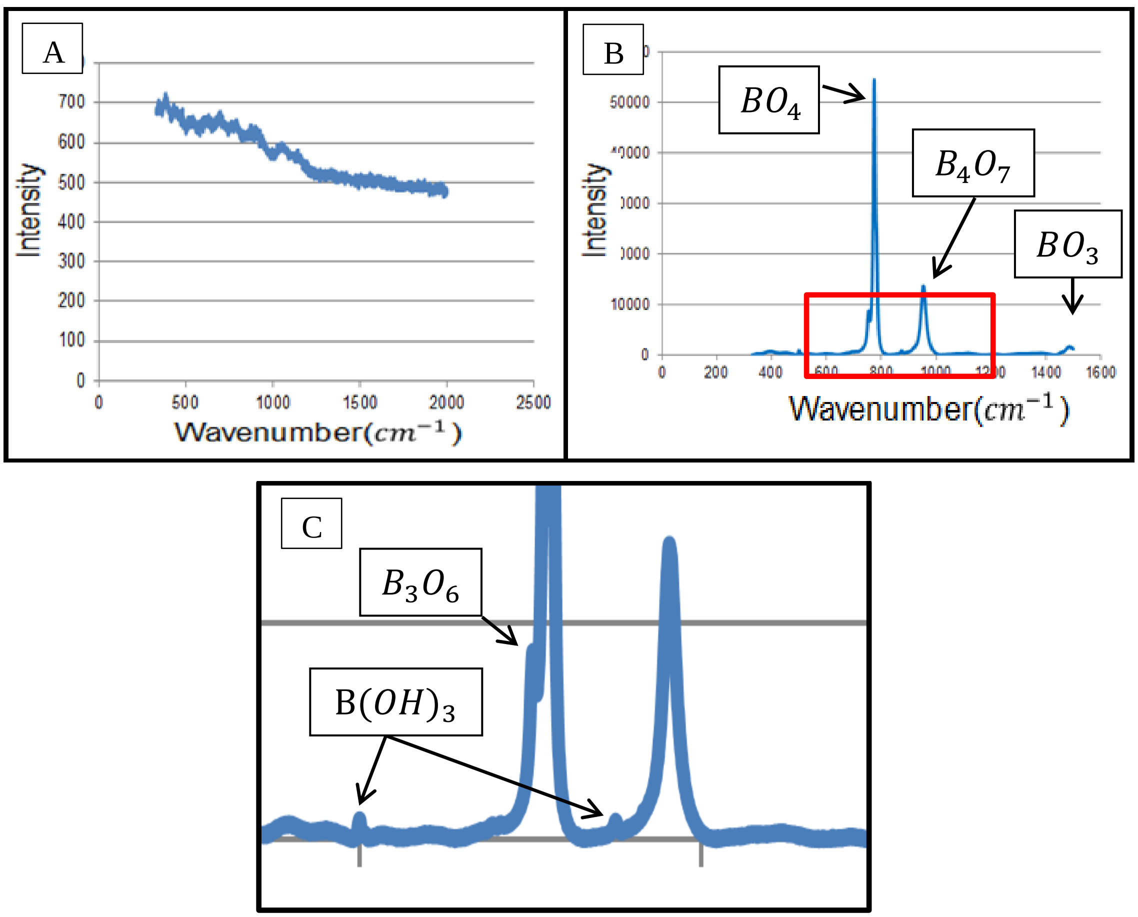

Figure 5-9. Raman spectroscopy test results

There were no certain peaks in the just amorphous boron powder, however when oxidized boron powder was reacted with water, there were all five peaks indicating that several materials were generated in the reaction. The result revealed that there were two small peaks for boric acid ($B(OH)_3$) about $500cm^-$ and $874cm^-$ wavelength as shown in figure B and C [56]. The highest peak is around $774cm^-$ wavelength which indicates the BO_4 structure [57]. The second highest peak is about $953cm^-$ showing the B_4O_7 structure. In addition, there was a peak that covered by the BO_4 peak, this peak was the B_3O_6 which is boroxol group about $753cm^-$ wavelength [58].

From this raman spectroscopy test result, it can be concluded that the reason of reduced COF and less wear rate in the tribometer experiments resulted from the boric acid that was generated by the oxidized amorphous boron powder with water reaction.

5. 5. Lubrication mechanism of boron powder in lubricants

It is obvious that the amorphous boron powder showed certain improvement in the lubricants: grease and oil. The oxidized amorphous boron powder increased the friction factor, and it reduced the COF in the tribometer experiments. Both results were clear that the boron powder positively affected on the lubricants' frictional behavior. The real mechanism for the grease tests was not fully understood in this research. However, it is believed that the boric acid, which generated from the reaction between boron oxide and water reaction, had a critical role in the emulsion tests. This boric acid has a lamella structure in a triclinic system that has weak hydrogen bonding between them. The weak hydrogen bonding between lamella structures is easy to shear and this allows deforming easily as in figure 5-10. As a result, the COF is reduced and less wear occurred, when boron powder was added to the emulsion.

In addition, according to the raman spectroscopy test results, there was some boroxol structures remaining, which has a plane structure, this may be good for the lubrication since oxidized amorphous boron powder added grease showed better friction factors in the API RP 7Al tests. Because the plane structure of the boroxol group would disperse the applied force by its area.

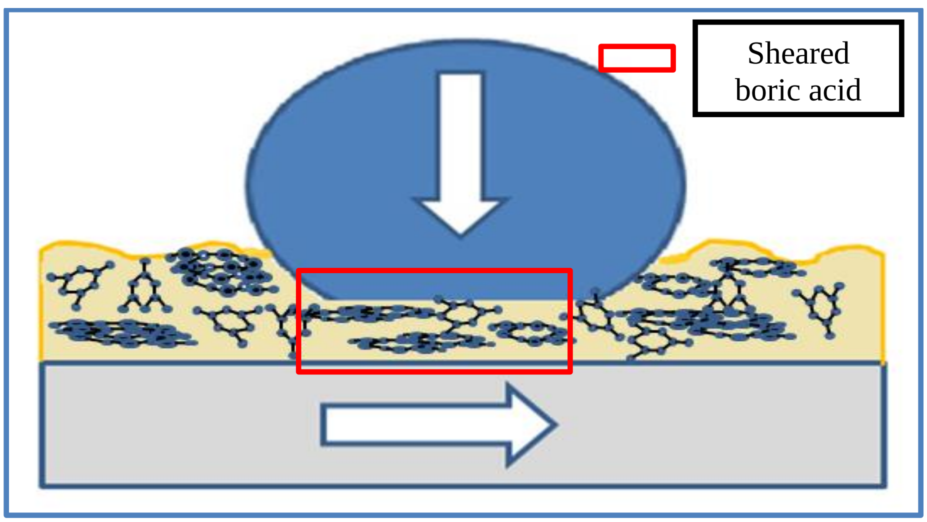

Figure 5-10. Boric acid and boroxol group in the mineral oil and water emulsion.

CHAPTER VI

CONCLUSIONS AND FUTURE RECOMMENDATIONS

6. 1. Conclusions

This research studied crystalline and amorphous boron powders' tribological performance in liquid and semi-solid lubricants. Two different experiments were conducted: API RP 7A1 thread compound test and Pin-on-Disk tribometer experiments.

There are three main findings in this research:

1) The crystalline boron powder decreased both greases' frictional behavior, while the amorphous boron powder increased the frictional behavior. In addition, the results were improved as increasing the boron powder's content. However, greases with emulsion showed slightly worse results compared to the oxidized amorphous boron powder added grease.
2) According to the Stribeck curve results, the oxidized amorphous boron added emulsion showed a lower coefficient of friction than just mineral oil. Furthermore, the oxidized amorphous boron added emulsion showed much less wear depth than the other two: just emulsion and mineral oil. Consequently, the calculated wear rate was the lowest in the oxidized amorphous boron added emulsion test.
3) Boric acid was generated in the boron added emulsion, and it is the main reason to reduce the coefficient of friction and wear in the experiments, since it has lamellar structure with hydrogen bonding between the molecules.

Results showed that the crystalline boron powder was not proper as lubricants' additive, while the oxidized amorphous boron powder increased the lubricants' frictional performance. This research suggests that the oxidized amorphous boron powder can be a lubricant's additive in both liquid and semi-solid compounds.

6. 2. Future recommendations

This research studied the impact of boron powder as an additive in lubricants. Even though different experiments were conducted with different compositions of boron powder, the actual composition of boric acid is not known. The experiments showed that the boric acid played a critical role in terms of lubricating property. A suggested focus for future research is to figure out how much boric acid was generated in the emulsion technique and how to increase the amount of boric acid in the same manner.

The actual mechanism of boron powder was not investigated in the API RP 7A1 tests. It is possible to obtain more information of the mechanism of different additives in grease with these tests. This study would expand the knowledge of lubricant additives' roles under a high load experiment.

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